

Advances in **ORGANOMETALLIC CHEMISTRY**

EDITED BY

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MADISON, WISCONSIN

VOLUME 5



1967

ACADEMIC PRESS

New York • London

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ACADEMIC PRESS INC.

111 Fifth Avenue, New York, New York 10003

United Kingdom Edition published by

ACADEMIC PRESS INC. (LONDON) LTD.

Berkeley Square House, London, W.1

LIBRARY OF CONGRESS CATALOG CARD NUMBER: 64-16030

PRINTED IN THE UNITED STATES OF AMERICA

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Organosulfur Derivatives of Silicon, Germanium, Tin, and Lead

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I. Introduction	2
II. Synthetic Methods	3
A. From Halides	3
B. From Organometallic Oxygen Compounds	10
C. From Organometallic Nitrogen and Phosphorus Compounds	13
D. Cleavage of Metal–Carbon Bonds	14
E. Fission of Metal–Metal Bonds	15
F. From Organometallic Hydrides	16
G. Synthesis of $R_3 M^{IV} SM^I$	18
H. Reactions of $R_3 M^{IV} XM^I$ ($X = S$ or Se)	19
I. By Heating Group IV Metal–Sulfur Compounds	21
J. Miscellaneous	22
III. Chemical Properties	23
A. Heat and Ultraviolet Light	23
B. Oxidation	23
C. Reduction	24
D. Reactions with Protonic Materials	24
E. Reactions with Covalent Halides	27
F. Reactions with Organolithium Compounds	34
G. Reactions with Metal Salts	35
H. Miscellaneous Reactions	37
IV. Physical Properties	38
A. X-Ray Diffraction	38
B. Electron and Neutron Diffraction	39
C. Infrared and Raman Spectroscopy	40
D. Nuclear Magnetic Resonance Spectroscopy	41
E. Dipole Moments	42
F. Bond Parachors	43
G. Magnetic Susceptibility	44
H. Molar Refractivities	44
V. Theoretical Considerations	44
A. Bond Strength	44
B. Electronegativity	45
C. π Bonding in Silicon Compounds	45
D. The Group IV Metal–Sulfur Compounds	47

VI. Industrial Interests	49
A. Silicon and Germanium	49
B. Tin	49
C. Lead	50
VII. Appendix: Tabular Survey (Tables 1-12)	51
References	83

I

INTRODUCTION

Whereas organotin and organolead compounds of sulfur were reported as early as 1860 (*121, 136, 137*), the corresponding germanium compounds were first made in 1932 (*42*), and rather surprisingly, organosilicon sulfides were not synthesized until 1950 (*71*).

It is pertinent here to point out some of the restrictions we have imposed on the scope of this article. We shall consider only the bivalent sulfur compounds of the tetravalent Group IV elements, thus excluding such extensive fields as the lead(II) mercaptides (*182*) and organometallic salts of sulfur oxyacids. No mention will be made of coordinated sulfur compounds of these elements, and isothiocyanates will only be considered where they illustrate a property of a sulfur compound under review. Silyl and germyl compounds and the thiohalogeno derivatives of the Group IV elements only appear where necessary for comparison purposes. The chemistry of the selenium and tellurium analogs of the sulfur compounds under consideration are fully reviewed.

Nomenclature is founded on the presently accepted convention of the tetravalent silicon and germanium compounds being silane and germane, with the tin and lead compounds based on the name of the metal (*109*). Thus, for example, the names of $(\text{CH}_3)_2\text{Si}(\text{SC}_2\text{H}_5)_2$ and $(\text{CH}_3)_2\text{Sn}(\text{SC}_2\text{H}_5)_2$ are, respectively, bis(ethylthio)dimethylsilane and bis(ethylthio)dimethyltin.

A number of excellent reviews exist on various aspects of the organic chemistry of the Group IV elements, and the reader is referred to these for wider discussion of the general properties of these materials: silicon (*29, 73, 74, 151, 153, 228*); germanium (*111, 177, 184, 185, 228*); tin (*109, 148, 149, 161, 182, 228, 235*); lead (*142, 254*).

II

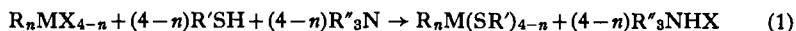
SYNTHETIC METHODS

A. From Halides

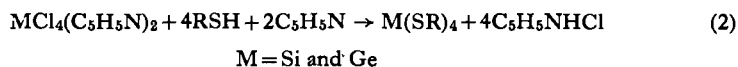
1. *Amine Method*

The condensation of thiols and halogenosilanes, with the direct elimination of hydrogen halide, has been reported to give a very small yield of a silicon-sulfur compound (114). The use of amine as a base for the removal of the hydrogen halide has, however, proved one of the most general methods available for the formation of sulfur bonds to silicon, germanium, tin, and lead.

This reaction has sometimes been noted to be reversible at elevated temperatures, and linear alkylthio derivatives of silicon (257), germanium (69, 107), tin (69), and lead (69) have all been prepared by this method.

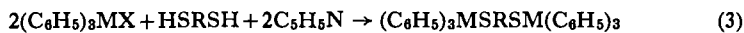
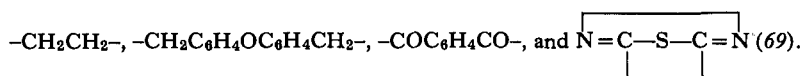


An analogous reaction involves the initial formation of the bis(pyridine)-metal tetrahalide complex which is subsequently treated with further pyridine in the presence of thiol (1, 107).



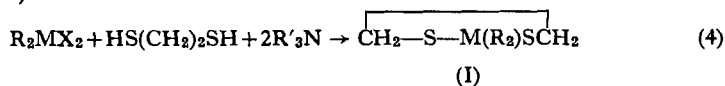
The use of hexamethyldisilazane as the base [see Eq. (1)] has been successful in the preparation of allylthiotrimethylsilane (P71), but the analogous reaction with *n*-butanethiol is reported to yield no silicon-sulfur derivative (140).

Utilization of dithiols or difunctional systems in these reactions can lead either to linear or cyclic compounds. Thus the interaction of bromotriphenylgermane and chlorotriphenyllead with dithiols yielded the linear compounds $(C_6H_5)_3MSRSM(C_6H_5)_3$, where R is



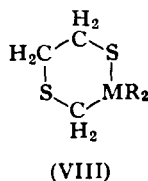
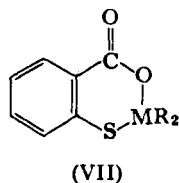
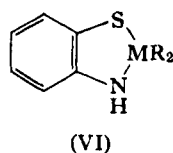
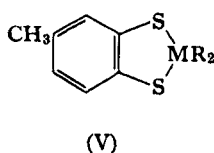
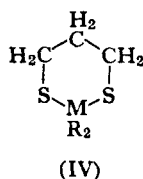
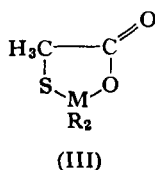
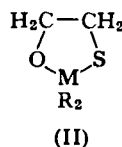
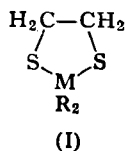
The earliest type of cyclic compound prepared by this method was from

the interaction of ethane-1,2-dithiol and the dialkyl or diaryl metal dihalides (69, 249, P55).

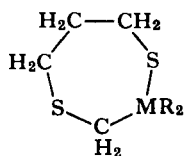


M = Si, Ge, Sn, and Pb

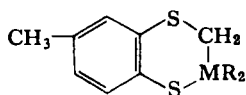
Variation of the difunctional thiol has resulted in the synthesis of a variety of novel heterocyclic compounds: (II) (243, 250); (III) (251); (IV) (247); (V) (248); (VI) (243, 252); (VII) (246, 251). Using the dichloride $\text{ClCH}_2\text{M}(\text{CH}_3)_2\text{Cl}$ (M = Si and Ge) has given a further modification to the ring systems produced: (VIII) (245); (IX) (245); (X) (244, 248). The two spirans (XI) and (XII) have also been prepared from the thiols and germanium tetrachloride in the presence of pyridine (69).



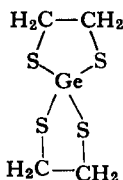
The reaction of hydrogen sulfide under similar conditions resembles that of the thiols, but leads to a wider variety of products. The triphenyl



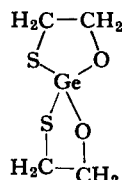
(IX)



(X)

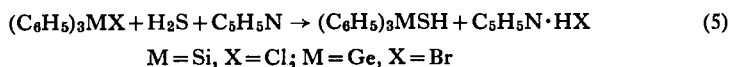


(XI)



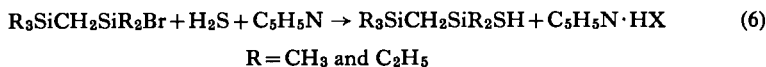
(XII)

halides of silicon (83) and germanium (69) react to give the thiol, whereas analogous tin and lead halides yield the hexaphenyldimetal sulfides.



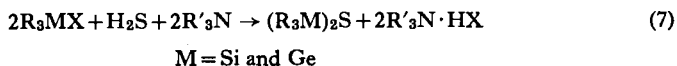
The germanium compound is reported to smell of hydrogen sulfide in the presence of moisture, just as triphenylmethanethiol does (236).

The 1-bromo-1,3-disilapropanes [see Eq. (6)] react in a similar way to give the silanethiols (158).

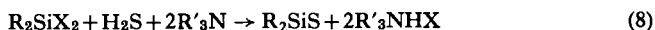


These thiols reacted with further bromide and pyridine to give the disilthianes $(\text{R}_3\text{SiCH}_2\text{SiR}_2)_2\text{S}$, such compounds being normally prepared directly from the halide and hydrogen sulfide.

Thus, halides of the type R_3MX react with hydrogen sulfide according to Eq. (7) to give the substituted disilthianes (63, 158) and digermthianes (7).

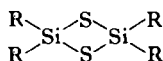


Dihalides of silicon react in a similar way to produce compounds of formula R_2SiS .

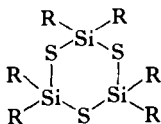


These materials have been isolated as dimers (XIII) (63, 82, 154) and trimers (XIV) (154, 163, P54).

The compound $(C_6H_{11})_2PbS$ has also been obtained by this route (96).

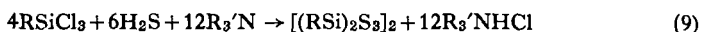


(XIII)

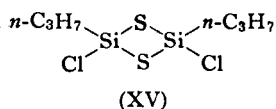


(XIV)

The analogous reactions of hydrogen sulfide and base with the trihalides in general produce the compounds $(RSi)_2S_3$. The compounds are claimed to be dimeric (82, 83).

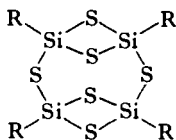


A deficiency of pyridine has given the compound (XV) (82) analogous to those produced from dihalides; it should possess separable geometrical isomers.

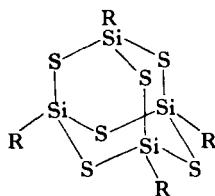


(XV)

It reacts further with hydrogen sulfide and pyridine to produce $(n-C_3H_7Si)_2S_3$ (82) and gives the slender evidence quoted that these trisulfides have structure (XVI) and not (XVII).

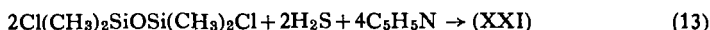
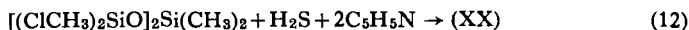
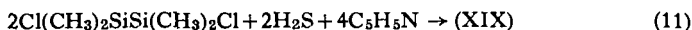


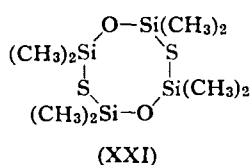
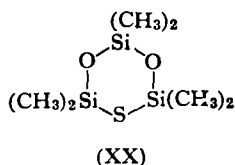
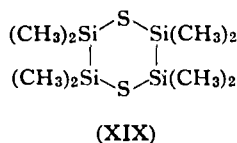
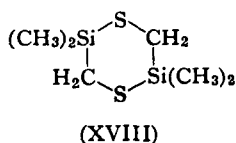
(XVI)



(XVII)

The ring systems (XVIII) (211), (XIX) (237), (XX) (30) and (XXI) (30), have been produced by the reactions recorded in Eqs. (10)–(13), respectively.



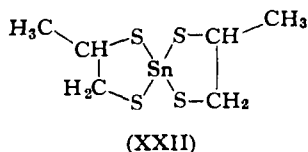


2. Aqueous Reactions

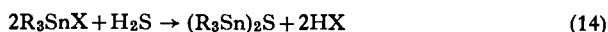
No silicon-sulfur bonds have been reported to form in aqueous media, but such reactions are known for germanium, tin, and lead. In this section, we describe the reactions of organometallic halides in aqueous solution with thiols and hydrogen sulfide. It is probable, however, that it is the hydrolysis products of the halides that react to form the metal-sulfur bonds.

Relevant organotin halides react with thiols in aqueous solution to produce compounds of the type $\text{R}_3\text{SnSR}'$, $\text{R}_2\text{Sn}(\text{SR}')_2$, and $\text{RSn}(\text{SR}')_3$ (14, 49). Stannic chloride and air-oxidized stannous chloride (258) both yield the tetraalkylthiotin compounds, $\text{Sn}(\text{SR})_4$. Trimethyllead chloride produces compounds of the type $(\text{CH}_3)_3\text{PbSR}$ with methane and ethane-thiols, while phenylselenol reacts with trimethyltin chloride in aqueous solution to give phenylselenotrimethyltin (6).

The ring compound (I) ($\text{M} = \text{Sn}$, $\text{R} = \text{Me}$) was prepared directly from ethane-1,2-dithiol and dimethyltin dichloride while the spiran (XI) ($\text{M} = \text{Sn}$) was prepared similarly from stannic chloride (14). The use of stannous chloride also led to (XI), presumably due to air oxidation. The interaction of stannic chloride and propane-1,2-dithiol has produced the substituted spiro compound (XXII) which possesses three geometrical isomers, each of which will have a pair of optical isomers. Recrystallized samples of (XXII) produce different crystalline species which do have different single-crystal X-ray patterns.



The reaction of hydrogen sulfide in aqueous and alcoholic solution with the relevant triorganotin halides produces the sulfides $(R_3Sn)_2S$ (14, 132).



Hexaphenyldilead sulfide has been prepared similarly (97), and the use of hydrogen selenide has given hexamethylditin selenide (132).

Numerous compounds of the general formula R_2MS have been made in aqueous and alcoholic solutions of various pH values by this method (14, 81, 92, 98, 99, 125, 132, 170, 186, 224, 230, P1, P53).



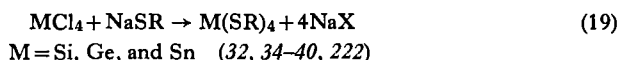
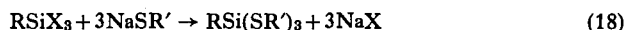
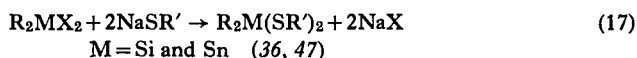
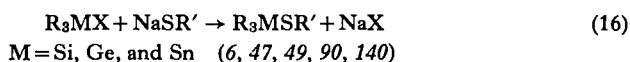
M = Ge, Sn, and Pb

These compounds have structures corresponding to those of the silicon compounds represented by (XIV) (58, 144, 174, 179). The use of hydrogen selenide similarly produces $[(CH_3)_2SnSe]_3$ (132).

Organotin trihalides react with hydrogen sulfide and selenide to give compounds of the formula $(RSn)_2X_3$ (X = S and Se) (132, 168).

3. Salts of Thiols and Hydrogen Sulfide

Sodium mercaptides have been extensively used in reactions with organo-metallic halides under varying conditions, and produce many different classes of Group IV metal-sulfur compounds.

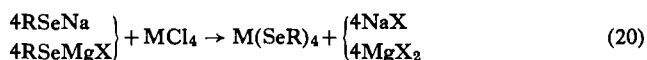


Despite the reported successful use of this method to prepare *n*-butylthio-trimethylsilane (140), other workers report that the reaction of chlorotrimethylsilane with the sodium salt of methanethiol produces, very remarkably, only hexamethyldisilthiane (107).

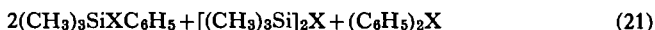
Corresponding reactions have been carried out with the mercaptides of magnesium and lead (2, 69, 107, 199, 222), the latter also being used to prepare lead(IV) thio compounds from a lead(IV) halide (106).

Cyclic and spiro compounds analogous to (I), (IV), (V), and (XI) have been produced from salts of bifunctional thiols with di- and tetrahalides of silicon, germanium, and tin (10, 32, 36, 39, 41, 175), while sodium, potas-

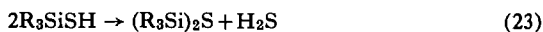
sium, and magnesium salts of selenols react with these tetrahalides affording complete halogen replacement (33).



Attempts to prepare phenylseleno- or phenyltellurotrimethylsilanes from the magnesium derivative resulted only in the isolation of hexamethyldisilselenane and tellurane (107). The disproportionation [Eq. (21)] has been proposed but this seems unlikely, since these compounds have been prepared by other methods and appear quite stable. It seems possible, therefore, that the "disproportionation" products reported are formed by some other mechanism.

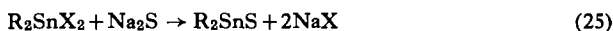
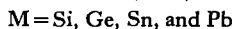
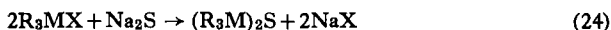


Hydrosulfides of lithium, magnesium, sodium, potassium, and ammonium all react with halogenotrialkylsilanes to give the silanethiol. These products subsequently disproportionate into the disilthiane and hydrogen sulfide (63).



Polymeric dialkyltin sulfides are produced from potassium hydrosulfide and dialkyltin dichlorides (101).

The reaction of sodium sulfide with organometallic halides of the Group IV elements proceeds for all four elements. However, silicon halides have to be heated in a bomb to high temperatures under anhydrous conditions (3), whereas other halides will react in aqueous or alcoholic solution (59, 62, 101, 108, 132, 224).

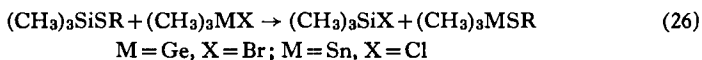


The reaction of sodium selenide with the relevant organometallic halide has led to the isolation of the following compounds: $(\text{R}_3\text{M})_2\text{Se}$, $\text{M} = \text{Si}$ and Sn ; $(\text{R}_2\text{SiSe})_2$; $(\text{R}_2\text{MSe})_3$, $\text{M} = \text{Si, Ge, and Sn}$ (204–207).

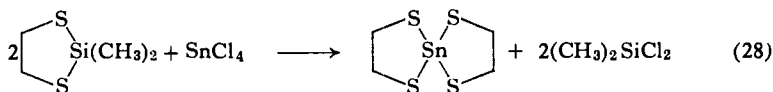
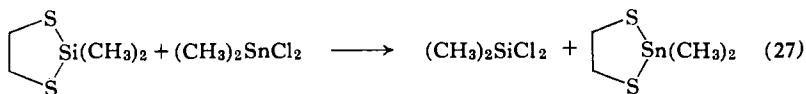
Passing various organosilyl iodides over mercury sulfides has given the corresponding disilthianes (78–80), while organometallic iodides of silicon, germanium, and tin react with silver sulfide to produce $(\text{R}_3\text{Si})_2\text{S}$ (71, 72), $[(\text{isoC}_3\text{H}_7)_2\text{GeS}]_2$ (23), and $[(\text{C}_6\text{H}_5)_3\text{Sn}]_2\text{S}$ (226).

4. Halide Metathesis

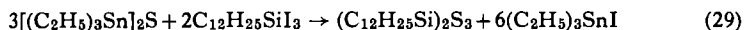
Halogenotrimethylgermane and -tin reacted with alkylthiotrimethylsilanes to cause elimination of halogenotrimethylsilane and yield germanium- and tin-sulfur compounds (6).



Using a similar technique, dichlorodimethyltin and stannic chloride have both reacted with 2,2-dimethyl-2-sila-1,3-dithiacyclopentane (11).



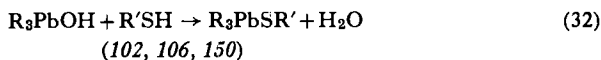
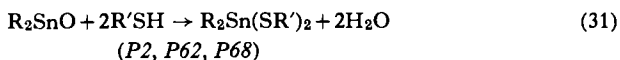
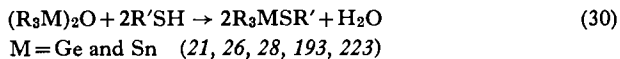
The metathesis of hexaethylditin sulfide and *n*-dodecyltriiodosilane yields triethyltin iodide and bis(*n*-dodecylsila)trisulfide, indicating that the direction of these reactions is not solely dependent on the Group IV metal-to-sulfur bond strength but also on other factors such as relative boiling points (25).



B. From Organometallic Oxygen Compounds

1. The Reaction of Thiols and Thioacids

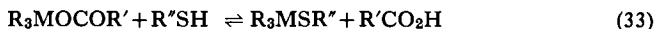
Thiols react with organometallic oxides and hydroxides of germanium, tin, and lead as depicted in Eqs. (30)–(32).



Water is often removed from these reaction mixtures by azeotropic distillation with toluene (P2, P28, P38).

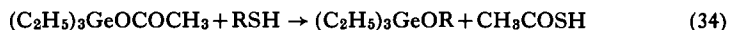
Thioacids similarly form metal-sulfur bonds with germanium (64), tin (P43, P94), and lead (103) in this way. In the case of lead, thioacids cause further cleavage of lead-carbon bonds.

The trialkyl germanium (26) and tin esters (195) of organic acids have been shown to form an equilibrium mixture with thiols.



The reaction can be driven from left to right if the organic acid formed is the most volatile component and can be removed from the equilibrium mixture.

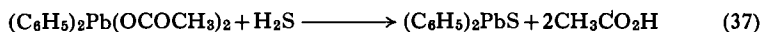
With *m*-toluenethiol and *o*-aminothiophenol, the reaction mixture yielded a small amount of thioacetic acid in addition to the normal products (26).



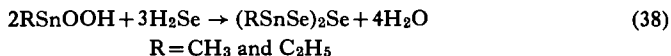
The organotin ester of perfluoroacetic acid is cleaved at the Sn—C as well as Sn—O bonds by thiophenol (195), which also eliminates ethanol from ethoxytrimethylgermane (6).

2. The Reaction of Sulfides and Selenides

Hydrogen sulfide reacts in an analogous manner with acetic acid solutions of "germanoic" anhydrides (42), organotin oxides (137), and organolead acetates with the formation of the Group IV metal-sulfur compound (144, 171).

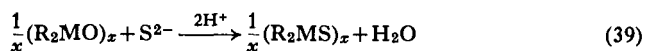


Hydrogen selenide reacts with "stannoic" acids to produce green precipitates of the selenide (232).



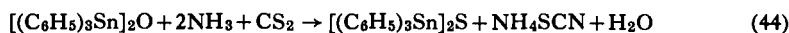
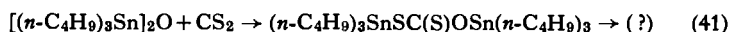
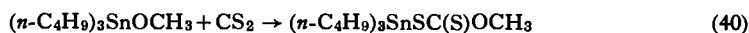
Organogermanium, tin, and lead oxides (179) all react with the sulfide ion in aqueous solution at varying pH, with the formation of the corresponding sulfides. The mechanism of the reaction of organotin oxides has been investigated and shown to proceed via a six-coordinate species.

Subsequent acidification leads to cleavage of tin-oxygen bonds and the formation of organotin-sulfur polymers.



3. The Reactions of Carbon Disulfide

Tin alkoxides (50) and oxides (50, 180, P45) and analogous lead compounds (108, 180) have been shown to react with carbon disulfide to form tin- and lead-sulfur bonds. The reaction is believed to involve addition of the tin-oxygen compound to the carbon-sulfur double bond. This intermediate has been isolated in some cases (50) but usually decomposed with the formation of the ditin sulfide and carbon oxysulfide (108, 180). In the presence of ammonia, carbon oxysulfide is removed as ammonium isothiocyanate (138).

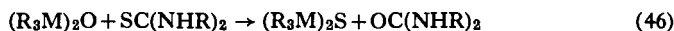


With benzylamine hydrobromide, however, hexaphenylditin oxide reacts according to Eq. (45), and subsequent heating causes decomposition to $(\text{C}_6\text{H}_5)_3\text{Sn}]_2\text{O} + \text{C}_6\text{H}_5\text{CH}_2\text{NH}_3\text{Br} + \text{CS}_2$



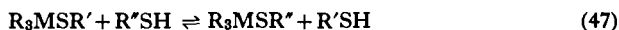
hexaphenylditin sulfide (138).

Triethyllead hydroxide (108) and hexa-*n*-butylditin oxide (67) react with thiourea and monosubstituted thioureas to yield the hexaalkylditin or lead sulfide, and probably urea.



4. Thiol Metathesis

This method involves the heating of a thio derivative of the Group IV metal with a thiol less volatile than the sulfur compound it is replacing, and depends on the same principles outlined for Group IV metal esters and mercaptans (Section II, B, 1). The method has been used for silicon (2, 3, 11), germanium (6, 26), tin (195), and lead (150) and in the case of tin, applied to perfluorothiophenol (6).



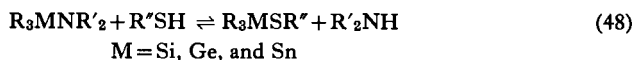
M = Si, Ge, Sn, and Pb

The reaction, normally slow, can be accelerated by using not only higher boiling mercaptans, but also more highly acidic ones. Thiophenol thus reacts more readily than many high-boiling aliphatic thiols. It would be interesting to compare the reactivity of some thioacids.

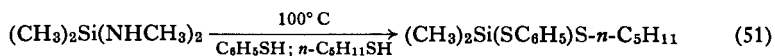
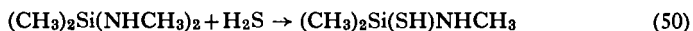
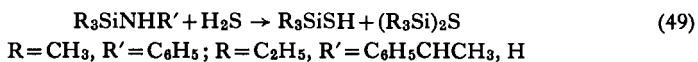
C. From Organometallic Nitrogen and Phosphorus Compounds

1. Thiols and Hydrogen Sulfide

Silicon–nitrogen compounds have been shown to react under reflux with a variety of thiols, to form the corresponding thiosilane. The energies of Si—N and Si—S bonds are similar, so an equilibrium is established which can only be displaced to the right if the amine formed is more volatile than the thiol used (2, 3, 11),



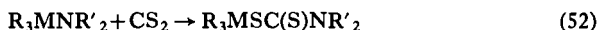
In the case of germanium and tin, however, the reaction is exothermic at room temperature, though no examination of thiols lower boiling than the amines has been made (6). The reaction can occur with elimination of a higher boiling amine, as hydrogen sulfide shows, and relative acidities may influence this (141, P111).



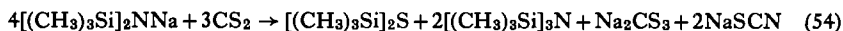
Hexamethyldisilazane and *N*-methylaminotrimethylsilane both react with (C₂H₅O)₂P(S)SH to produce a small amount of the trimethylsilyl ester (44) while *n*-butanethiol yields *n*-butylthiotrimethylsilane by cleaving the silicon–phosphorus bond in di-*n*-butyltrimethylsilyl phosphonate (115).

2. Carbon Disulfide

Silicon–nitrogen and tin–nitrogen compounds add to the carbon–sulfur double bond to produce thiocarbamates (54, 55, 85). In some cases, these have been isolated (55), but normally they decompose on heating to the starting materials (Si; 54) or a ditin sulfide (Sn; 85).



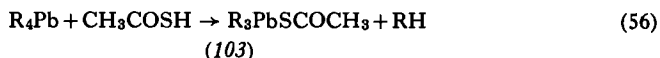
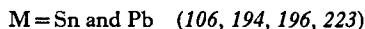
The sodium salt of hexamethyldisilazane reacts with carbon disulfide in two different ways, depending on the relative proportions, but both yield hexamethyldisilthiane (238).



D. Cleavage of Metal–Carbon Bonds

1. Fission by Thiols and Thioacids

Under varying conditions, thiols and thioacids have been found to cause fission of tin- and lead-carbon bonds, as illustrated in Eqs. (55)–(57).

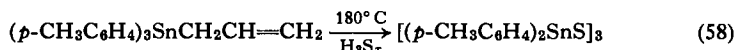


(103)



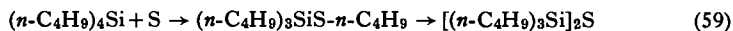
(103, 106)

Hydrogen polysulfide is reported to react with allyltri-*p*-tolyltin to give the trimeric diaryltin sulfide (221).



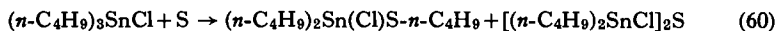
2. Fission by Elemental Sulfur and Selenium

Tetra-*n*-butylsilane reacts with sulfur at elevated temperatures to produce hexa-*n*-butyldisilthiane. The formation of *n*-butylthiotri-*n*-butylsilane is postulated as an intermediate in this reaction (210).

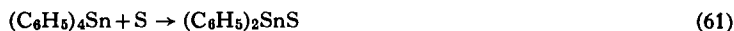


The corresponding reaction with tetra-*n*-butylgermane at 210° C produced more extensive fission with polymeric di-*n*-butylgermanium sulfide as an end product (210).

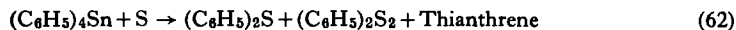
The reactions of sulfur with organotin compounds show progressive fission of tin-carbon bonds as exemplified by Eqs. (60)–(62).



(213)

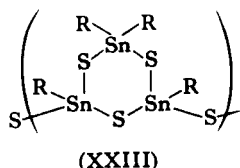


(203)



(52, 53, 178)

Under carefully controlled conditions, the reactions of alkyl and aryl tin compounds with sulfur have produced a variety of polymeric materials typified by (XXIII) (203, 208).

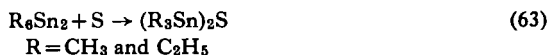


Selenium and tetraphenyltin yield phenylselenotriphenyltin, whereas tetra-*n*-butyltin undergoes more extensive cleavage to give trimeric di-*n*-butyltin selenide (209). Tetraethyllead is reported to yield hexaethyldilead sulfide from sulfur, with ethylthiotriethyllead postulated as an intermediate (108).

E. Fission of Metal–Metal Bonds

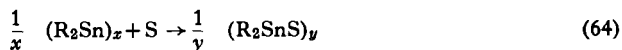
1. Sulfur

Hexaalkylditins will add sulfur across the tin–tin bond to form hexaalkylditin sulfides (126, 203).

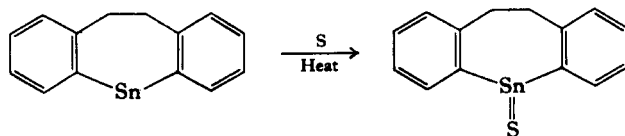


Hexaphenyldilead reacts similarly but with the formation of tetraphenyllead and diphenyllead sulfide as by-products (127).

“Dialkyl and diaryl tins” have been shown to be polymeric and possess tin–tin bonds. They react with sulfur to yield polymeric diorganotin sulfides (134, 125).

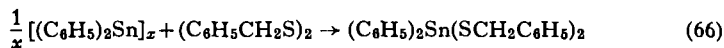


5-Stannadibenzocycloheptadiene is reported to add sulfur to the tin atom, with the formation of the monomeric compound indicated, which possesses a tin–sulfur double bond (134).

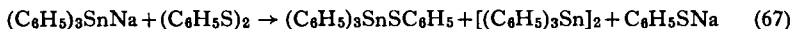


2. Disulfides

"Diphenyltin" reacts with dibenzyl disulfide with cleavage of the sulfur-sulfur bond and formation of bis(benzylthio)diphenyltin (135).

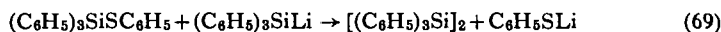


Triphenyltin sodium cleaves the S—S bond in diphenyl disulfide in a similar manner (49).

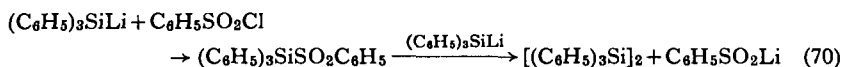


3. Diphenyl Sulfide, Sulfoxide, and Sulfone (256)

Diphenyl sulfide is cleaved by triphenylsilyllithium and subsequent carboxylation yields hexaphenyldisilane, benzoic acid, and thiophenol. This indicates that phenylthiotriphenylsilane must be formed as an intermediate, which undergoes the further cleavage indicated.



Triphenylsilyllithium also reacts with benzenesulfonyl chloride and diphenyl sulfone. The former yields hexaphenyldisilane and lithium benzene sulfinate, while the latter gives tetraphenylsilane, the sulfinate, and silanol.

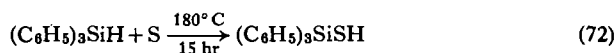


Triphenylsilylpotassium and diphenyl sulfoxide yield hexaphenyldisilane (12%), hexaphenyldisiloxane (21%), and tetraphenylsilane (27%).

F. From Organometallic Hydrides

1. Sulfur

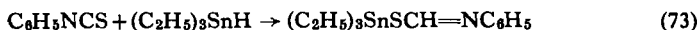
Sulfur has been shown to insert directly into the Si—H bond of triphenylsilane at 180° C in decalin (46, 61).



2. Phenyl Isothiocyanate

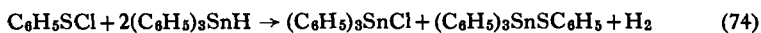
Both triethyl and triphenyltin hydride are reported to add to the C—S double bond in phenyl isothiocyanate as indicated (160), though subsequent

work tended to disprove this (159). Triphenyltin hydride also leads to the formation of hexaphenylditin and hexaphenylditin sulfide as well as anilines and phenyl isocyanide (146).



3. Sulfur Halides

Traces of hexaethylditin sulfide are produced from the reaction of triethyltin hydride with disulfur dichloride (24), while phenylsulphur monochloride chlorinates the Sn—H bond in triphenyltin hydride. This reacts with thiophenol formed by reduction of the halide to yield phenylthiotriphenyltin (165).



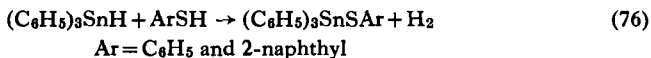
4. Thiols

Organosilanes, germanes, and stannanes are all reported to react with mercaptans under varying conditions with the evolution of hydrogen.

Thus, triphenylsilane reacts with *p*-toluenethiol at 225° C over a period of 5 days to yield *p*-tolylthiotriphenylsilane in 69% yield (91, 255).



Similarly, triethylgermane reacts with *n*-butanethiol under reflux in the presence of a platinum catalyst to give a 75% yield of *n*-butylthiotriethylgermane after 72 hours (143). Aryl mercaptans cleave the tin-hydrogen bond with subsequent formation of a Sn—S bond (165).

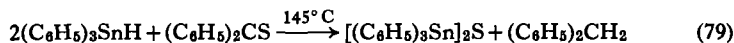
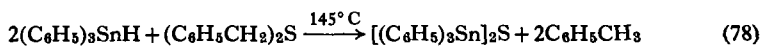


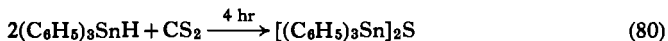
With allyl mercaptan however, triphenyltin hydride reacts to yield hexaphenylditin sulfide, indicating cleavage of the C—S bond (162).



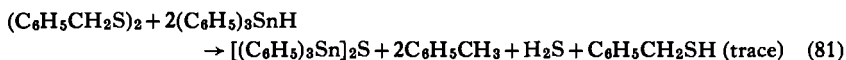
5. Miscellaneous Sulfur Compounds

Carbon-sulfur bonds are cleaved by triphenyltin hydride in dibenzyl sulfide, thiabenzophenone, and carbon disulfide (165). Hexaphenylditin sulfide was produced in each case, though in only 13% yield from carbon disulfide.





With dibenzyl disulfide, a similar cleavage of C—S bonds occurs, with the formation of hexaphenylditin sulfide, but with diphenyldisulfide only the S—S bond is broken.

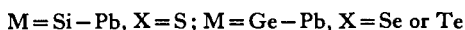
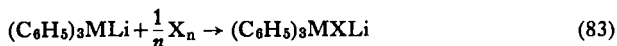


G. Synthesis of $\text{R}_3\text{M}^{\text{IV}} \text{SM}^{\text{I}}$

Four methods have been reported for the preparation of these compounds and all but one involve the use of a Group IV metal-sulfur compound as intermediate. The other involves the reaction of an organometallic Group I derivative with sulfur, selenium, or tellurium.

1. Group I Organometallic Compounds with Group VI Elements

Lithium triphenyl derivatives of all the Group IV elements react with sulfur on heating in tetrahydrofuran to yield the lithium derivative of the thiol (215, 217, 219, 220). The germanium, tin, and lead compounds have also been shown to react with selenium and tellurium in a similar way (215, 218–220). The mechanism postulated is a stepwise nucleophilic attack on the Group VI element by the $(\text{C}_6\text{H}_5)_3\text{M}^-$ ion.

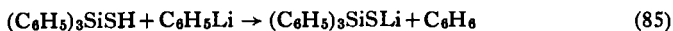
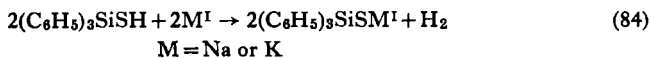


The tin-sulfur compound is reported to be dimeric (216).

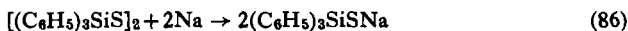
Diphenyltindilithium reacts with sulfur in a similar manner to produce the lithium salt of the dithiol $(\text{C}_6\text{H}_5)_2\text{Sn}(\text{SLi})_2$ (217).

2. Thiol and Group I Metal

Triphenylsilanethiol has been shown to react with sodium and potassium (46), with evolution of hydrogen and formation of the alkali metal derivative of the thiol. Lithium phenyl reacts similarly to produce benzene.



The sodium compound has also been prepared from hexaphenyldisildithiane and sodium metal.



3. $[(\text{CH}_3)_2\text{GeX}]_3$ and Methylithium ($X = \text{S}, \text{Se}$)

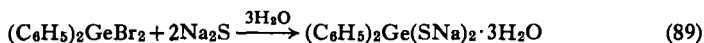
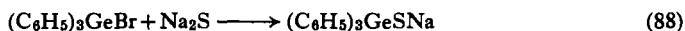
The trimers of dimethylgermanium sulfide (189) and selenide (190) both react with methylithium to produce the lithium derivatives of trimethylgermanethiol and selenol.



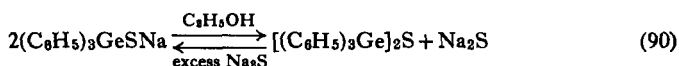
In the case of the selenium ring, an excess of methylithium yields tetramethylgermane (190).

4. Sodium Sulfide

Ethanollic sodium sulfide has been shown to react with bromotriphenylgermane (104, 105, 107), as has an aqueous solution with dibromodiphenylgermane (104). The sodium derivatives produced are hygroscopic crystalline solids.

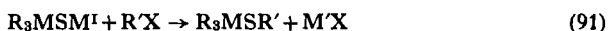


The monosodium salt decomposes in refluxing anhydrous ethanol to sodium sulfide and hexaphenyldigermthiane, but addition of more sodium sulfide reverses the reaction.



H. Reactions of $\text{R}_3\text{M}^{\text{IV}}\text{XM}^{\text{I}}$ ($X = \text{S}$ or Se)

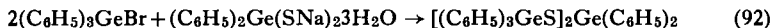
Alkali metal derivatives of the thiols of silicon, germanium, tin, and lead have all been shown to react with simple organic halides to produce the corresponding organothio derivative.



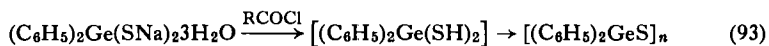
Lithium and sodium salts of triphenylsilanethiol react with alkyl, aryl, and silyl halides, and it is worth noting that although the sodium salt reacts with phenyl and silyl halides, the lithium one fails to do so with iodobenzene or silyl chlorides (46, 89).

The lithium salt of triphenylgermanethiol yields the thioester with

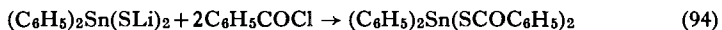
benzoyl chloride (219), while the sodium salt reacts with similar organic halides at room temperature in benzene (105). Dibromodiphenylgermane reacts to produce bis(triphenylgermylthio)diphenylgermane $[(C_6H_5)_3GeS]_2Ge(C_6H_5)_2$, also produced from bromotriphenylgermane and the disodium salt of diphenylgermanedithiol, which, with methyl iodide, yields crude bis(methylthio)diphenylgermane (104).



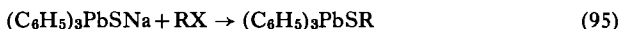
This salt has been isolated in the form of its trihydrate, and reaction with benzoyl and *p*-nitrobenzoyl chloride results in the isolation of dimeric and trimeric diphenylgermanium sulfide, due to the presence of water (104).



The dilithium derivative of diphenyltindithiol reacts with benzoyl chloride to produce bis(thiobenzoyl)diphenyltin, unlike the case of germanium (217).



Although only one triphenyltin compound, $(C_6H_5)_3SnSCOC_6H_5$, has been prepared by this method (216), many lead compounds have been made (106).

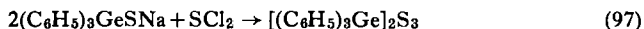


Lithium derivatives of triphenylgermanium, tin, and lead thiols react with the triphenyl halides of these three metals to produce the corresponding sulfides as crystalline solids (215, 216, 218–220).

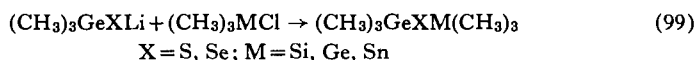
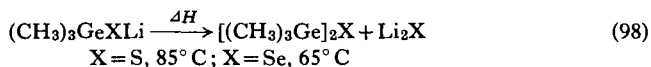


The sodium salt of the tin thiol reacts with bromotriphenylgermane similarly (104). Several selenium and tellurium analogs have been isolated in like manner (215, 218–220).

The sodium derivative of triphenylgermanethiol is reported to react with sulfur dichloride, yielding a trisulfide, but no experimental evidence is given (105).



Cleavage of hexamethylcyclotrigermthiane and -selenane with methyl-lithium has already been described. The lithium derivatives formed decompose on warming, and react with chlorotrimethylsilane, -germane, and -tin at room temperature (189, 190).



All these sulfides have been isolated but the mixed ones disproportionate on heating into the symmetrical derivatives. The selenides decompose in a similar way, the tin compound even on slight warming.

1. By Heating Group IV Metal-Sulfur Compounds

1. Alone

The result of heating several sulfur and selenium compounds has already been mentioned in the preceding section but the two most common forms of decomposition involve removal of hydrogen sulfide, and ring oligomerization.

The former has been investigated for organosilanethiols, and results in the formation of disilthianes (63, 141).



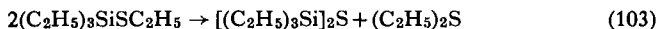
Both hexaphenyl and hexamethylcyclotrisilthiane (154, 163) have been shown to oligomerize on heating, with reduction of ring size.



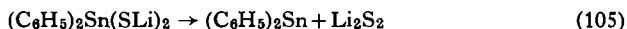
Tetramethylcyclodisilselenane, however, will expand its ring size at room temperature (204, 207).



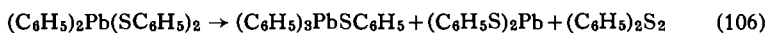
Heating ethylthiotriethylsilane at 300°C has resulted in the formation of diethyl sulfide and hexaethylidisilthiane, while at 350°C , bis(ethylthio)-diethylsilane decomposes to tetraethylcyclodisilthiane (199).



The thermal decomposition of thiogermanes has not been investigated but the phenyltin analogs of the silanes just mentioned yield polymeric diphenyltin sulfide both alone, and with sulfur (203). The dilithium derivative of diphenyltindithiol decomposes to polymeric diphenyltin and dilithium disulfide (217).



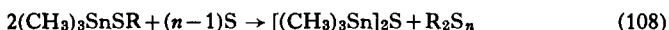
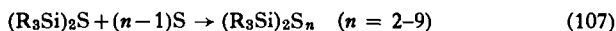
Bis(phenylthio)diphenyllead produces divalent lead mercaptides on heating, as well as phenylthiotriphenyllead and diphenyl disulfide (109).



The trends indicated in these results tend to support the idea that the strength of the Group IV metal-carbon bond decreases with increasing atomic weight, and consequently alkyl and aryl group migration tends to occur.

2. With Sulfur

Hexamethyl- and hexaethyldisilthianes are reported to react with sulfur at 200°C to yield a mixture of polysulfides (198, P47), while a similar reaction with alkylthiotrimethyltins produced hexamethylditin sulfide and dialkyl polysulfides (14).



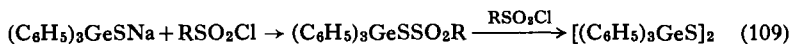
J. Miscellaneous

1. Oxidation

The sodium derivatives of thiols of triphenylsilane and germane have been oxidized by iodine (46) and hydrogen peroxide (104), respectively, to yield the disulfides, also produced from the germanethiol and iodine (104).

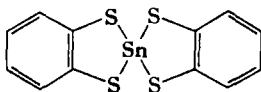
2. Sulfonyl Halides

Similar oxidations to those above are reported with methane- and *p*-toluenesulfonyl chlorides for the germanethiol salt (104, 105) and are reported to proceed via a sulfonylthiogermane (104).



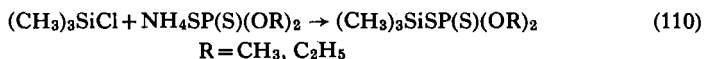
This type of reaction is observed in organic chemistry for sodium mercaptides and sulfonyl chlorides (86).

Benzene-1,2-disulfonyl chloride yields a red, insoluble compound with tin in hydrochloric acid (172). This is reported to be a spiran (56).



Disulfides also react with tin in concentrated hydrochloric acid to give tetraorganothio derivatives of tin (258).

Chlorotrimethylsilane and the ammonium salt of *O,O*-dimethyldithiophosphate react in acetone. A 76% yield of the corresponding Si—S compound was isolated, and the diethyl compound was prepared similarly (84).



III

CHEMICAL PROPERTIES

A. Heat and Ultraviolet Light

The thermal stability of silicon-sulfur compounds has already been partially reviewed in the light of its use as a synthetic method for preparing organo Group IV metal-sulfur compounds.

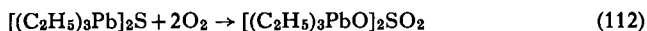
The decomposition of the two ethylthioethylsilanes mentioned goes completely to tetraethylsilane and silicon disulfide at high temperature (199), as does that of tetraethylthiosilane. Careful control of this latter case can give $[(\text{C}_2\text{H}_5\text{S})_2\text{SiS}]_2$ and $(\text{C}_2\text{H}_5\text{S})_2\text{Si}(\text{S}_2\text{Si})_{21}(\text{SC}_2\text{H}_5)_2$. Other esters yield silicon disulfide and, in the presence of sulfur, tetraethylthiosilane yields ethyl polysulfides (200).



Dibutyltin sulfide is reported to decompose at higher temperatures than the corresponding oxide (43); tetraalkenylthiotins polymerize in sunlight (36) while hexamethylcyclotritin selenide (132) and organo lead-sulfur compounds (62, 102) are all reported to be photosensitive.

B. Oxidation

Attempts to oxidize Group IV metal-sulfur compounds have in the main, proved inconclusive. Air oxidation is reported not to affect simple alkylthiosilanes and germanes (107), though hexamethylditin sulfide (126), and the lithium derivatives of triphenyltinthiol, selenol, and tellurol (215) are all air-sensitive. Hexaethyldilead sulfide is slowly oxidized by air to the sulfate (62).



Oxides of nitrogen are reported to cleave the Si—S bond in silthianes (100), though sulfones are said to be formed at -20°C (198).

Oxidation of *p*-tolylthiotri-*o*-tolylsilane with potassium permanganate results only in the isolation of the silanol (90), though tetraethylthiosilane is reported to yield the tetrasulfone. This decomposes above -40°C into silica.



Similar oxidation of the series $(C_2H_5S)_nSiCl_{4-n}$ ($n=1-3$) shows increased stability of the sulfone with chlorine content (198).

Polymeric dimethylgermanium sulfide has been oxidized by both hydrogen peroxide and dilute sulfuric acid to octamethylcyclotetragermoxane, although this may be hydrolysis (P1, P53).

C. Reduction

Little work has been conducted in this field. In dioxane, lithium hydride reduces hexamethyldisilthiane to the hydride (72), while lithium aluminum hydride preferentially reduces the Si—Cl bond in alkylthiochlorosilanes. Polymeric dimethylgermanium sulfide is reduced to dimethylgermane by hydrochloric acid and zinc amalgam (240).

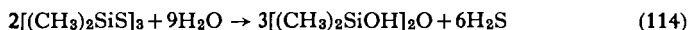
D. Reactions with Protonic Materials

1. Compounds Containing the O—H Bond

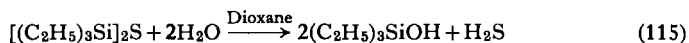
In general, the stability of the Group IV metal—sulfur bond relative to the Group IV metal—oxygen bond increases with the atomic weight of the Group IV element. This is apparent from the synthetic section which considers the preparation of Group IV metal—sulfur compounds from their oxygen derivatives. Consequently the reactions of hydroxy compounds is limited mainly to silicon, though some work has been done with germanium and tin.

Aqueous hydrolysis under neutral and alkaline conditions proceeds readily for Si—S compounds. The products vary, depending on the pH of the solution and the Si—S compound considered, but normally the siloxane is isolated (2, 80, 107, 211, 244, 247–249). In certain cases, however,

it has proved possible to isolate the silanol (90, 91, 255), and the alkaline hydrolysis of hexamethylcyclotrisilthiane leads to *sym*-tetramethyldi-hydroxydisiloxane (P54).



It is probable that hydrolysis of Si—S bonds yields the silanol initially, but that this dehydrates intermolecularly in acid solution due to protonation of the oxygen atom weakening the Si—O bond (72).



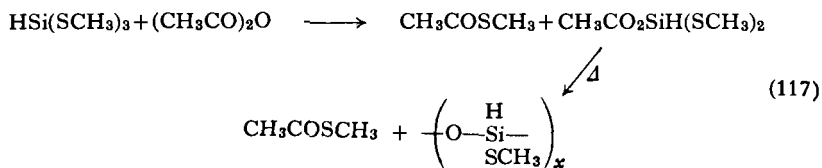
Tetraalkylthiosilanes are stable to hot concentrated hydrochloric acid and hot water, but not alkali (37).

Alcohols react similarly to produce alkoxyasilanes which are often difficult to prepare by other methods, due to the formation of troublesome alcohol-alkoxyasilane azeotropes (2, 3, 211).

Organic acids cleave the Si—S bond to form silyl esters (3), as does acetic anhydride (257).



The reaction of trimethylthiosilane with acetic anhydride initially involves ester formation but the silyl compound deesterifies to yield a polymer.



From the little work that has been done on the hydrolysis of germanium-sulfur compounds, it appears that an acidic aqueous solution is required to promote hydrolysis. Thus polymeric dimethylgermanium sulfide produces octamethylcyclotetragermoxane (186, P1, P53) while hot water will hydrolyze the Ge—Se bond in $[(\text{CH}_3)_2\text{GeSe}]_3$ (204).

Several germanium heterocycles are hydrolyzed to the germoxane under neutral conditions (244, 247, 249), though other work indicates complete lack of hydrolysis (107). Benzoic acid reacts with furfurylthiotriethylgermane, but this has not been investigated further (26).

The tin-sulfur bond has been hydrolyzed by strong aqueous alkali in various linear and cyclic compounds (175, 213) to produce organotin oxides,

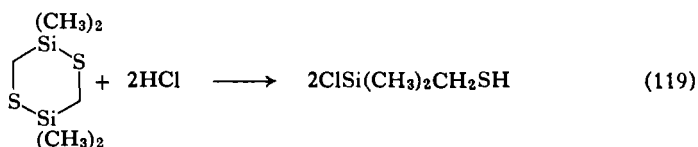
but two tin-sulfur compounds are reported as water-sensitive (132, 249), e.g.,



Acetic acid reacts with isopropylthiotriethyltin to yield the tin ester (195), while hydrogen sulfide is readily released by dissolving hexamethylditin sulfide in mineral acids (126), which also readily cleave the Pb—S bond (106). In addition the lead-carbon bond is readily broken by thioacids, as previously mentioned.

2. Hydrogen Halides

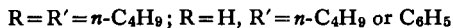
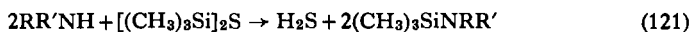
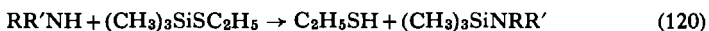
Dry hydrogen chloride reacts readily with the silicon-sulfur bond in a variety of heterocyclic compounds (211, 242, 245) to yield hydrogen sulfide or the thiol, e.g.,



The tin-sulfur (56) and lead-sulfur (102) bonds react similarly, while hydrogen iodide cleaves the Si—S bond in *sym*-dimethyldisilthiane (78).

3. Amines

Primary and secondary amines react with both ethylthiotrimethylsilane and hexamethyldisilthiane to produce the corresponding aminosilane. This illustrates the approximately equal replacement tendencies of alkylthio and alkylamino groups in silanes; the reactions of thiols with aminosilanes have already been described.



There is evidence to indicate that the amination of hexamethyldisilthiane produces trimethylsilanethiol as an intermediate (3).

4. Thiols

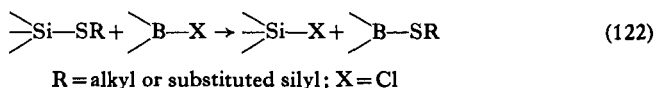
The reactions of Group IV metal-sulfur compounds with thiols have already been reviewed as a synthetic method, and shown to apply to all the Group IV elements considered.

E. Reactions with Covalent Halides

Extensive investigations have been conducted on the reactions of covalent halides with the Group IV metal-sulfur compounds and these are summarized by considering the halides according to their group classification.

1. Group III

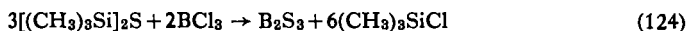
Boron trifluoride and trichloride both react with *sym*-dimethyldisilthiane at 100° C, though no adduct was formed at low temperatures, indicating lack of donor activity compared with dimethyl sulfide. The products of decomposition were polymeric and unidentified (78). Cleavage of the Si—S bond in fully substituted compounds by boron halides has, however, proved a most useful synthetic technique for boron-sulfur compounds (10). In general, the reactions are simple metathetical ones, and are often exothermic.



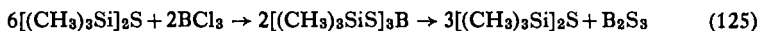
Alkylthiosilanes have been shown to partially or fully exchange with the chlorine in boron and phenylboron chlorides, e.g.,



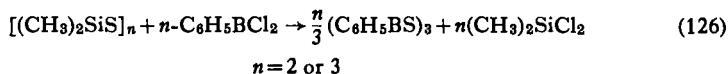
Similarly, complete cleavage of all Si—S bonds in hexamethyldisilthiane can be achieved with boron trichloride, to yield boron trisulfide.



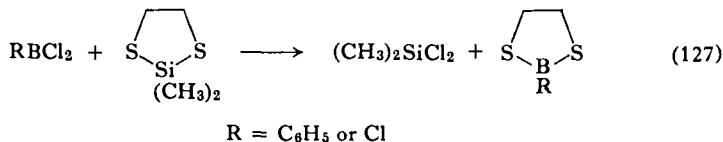
The slow addition of boron trichloride to the silthiane (ratio 1:3) resulted in the isolation of what was probably tris(trimethylsilylthio) borate. This decomposed on warming to the silthiane and boron trisulfide.



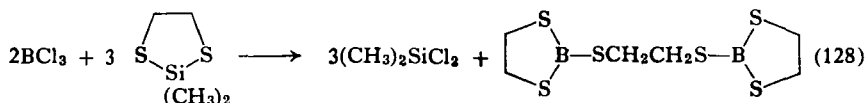
Both hexamethylcyclotrisilthiane and tetramethylcyclodisilthiane react with phenylboron dichloride to yield *B*-triphenylborsulfole as the only boron-sulfur product.



Both boron trichloride and phenylboron dichloride react with 2,2-dimethyl-2-sila-1,3-dithiacyclopentane in the ratio 1:1 to produce the corresponding boron heterocycle.



In the case of boron trichloride, excess silacyclopentane causes complete substitution at the boron, and the product is the bis(cycloborathio) derivative of ethane (11).

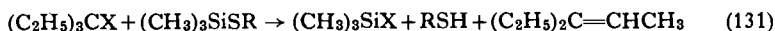
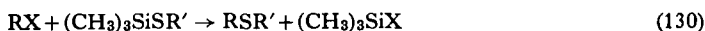


Boron trichloride reacts with the Sn—S bond in a similar way and has led to the isolation of tri-*n*-butyl trithioborate (15).



2. Group IV

a. *Carbon*. Alkyl chlorides, bromides, and iodides all cause simple metathetical cleavage of the silicon-sulfur bond in alkylthiosilanes (2, 8), with formation of the corresponding silyl halide and dialkyl sulfide. The reaction rate increases with the atomic weight (8) but an attempt to speed up the reaction rate by increasing the inductive effect of the alkyl group resulted in olefin and hydrogen halide formation. Cyclohexyl iodide produced a similar elimination but the bromide did yield the sulfide. Iodobenzene failed to react despite prolonged refluxing.

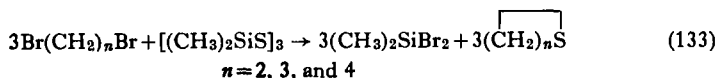


This method is useful for preparing unsymmetrical sulfides.

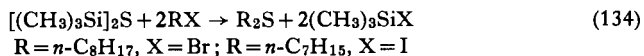
Methylene iodide reacts in a similar manner to produce the bis(alkylthio)-methane.



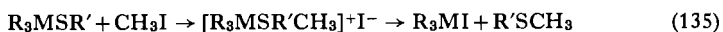
1,2; 1,3; and 1,4-Terminal dibromoalkanes have been shown to react with hexamethylcyclotrisilthiane to yield the thiacycloalkane and dibromodimethylsilane



while both hexamethyldisilthiane and hexamethylcyclotrisilthiane react with alkyl halides to yield the symmetrical sulfides, e.g.,

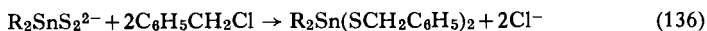


In considering the reactions of methyl iodide with compounds containing Group IV metal-sulfur bonds, there appears to be disagreement over the mode and rate of reactions. Thus *sym*-dimethyl- and tetramethyldisilthianes are reported not to react with it (78, 80), alkylthiotrimethylsilanes are cleaved even at room temperature (8, 107), as are compounds containing sulfur bonded to germanium (107), tin (14, 258), and lead (106). Sulfonium adducts are postulated

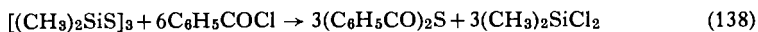
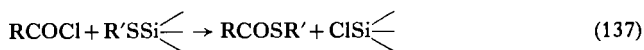


as intermediates but whether they can be isolated, or only have a transitory existence is still a subject of speculation (2, 8, 14, 106, 107).

Anionic organotin sulfides react with benzyl chloride to produce the dibenzylthio derivative (179).

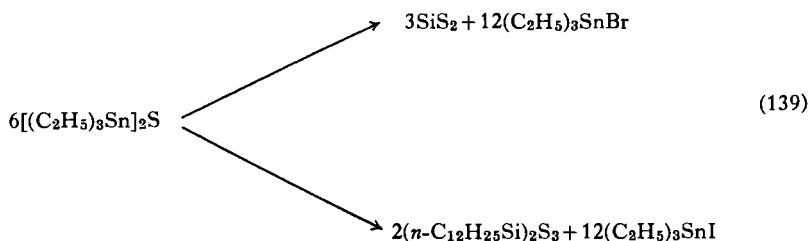


Chlorides of organic acids also cleave the silicon-sulfur bond with formation of thioester (4, 257).

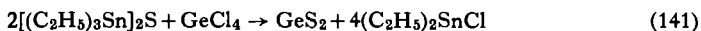
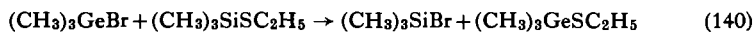


b. *Silicon*. There is no report of the reaction of a silyl halide with a silicon-sulfur compound, though several reactions with germanium- and tin-sulfur compounds have been investigated.

β -Naphthylthiotriethylgermane reacts with dichlorodiphenylsilane to yield 25% of chlorotriethylgermane (26) while the reaction of hexaethylditin sulfide with silicon tetrabromide and *n*-dodecyltriiodosilane yields the corresponding silyl sulfide and halogenotin in very good yields (25).

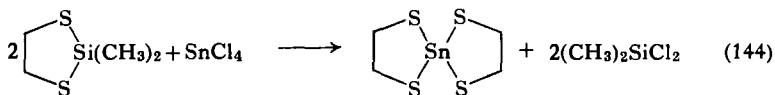
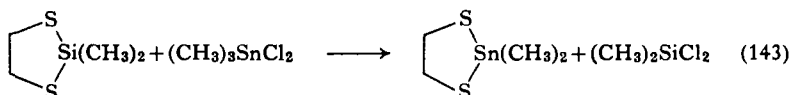
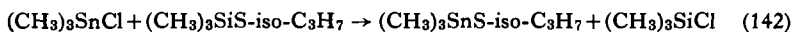


c. *Germanium*. Halogenogermanes have reacted with both silicon and tin-sulfur compounds. Ethylthiotrimethylgermane has been prepared in reasonable yield from the corresponding silane and bromotrimethylgermane (6), while germanium tetrachloride reacts with hexaethylditin sulfide to produce germanium disulfide (25).



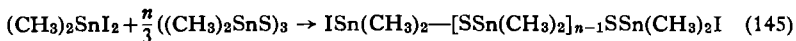
d. *Tin*. A variety of organotin halides and stannic chloride have been shown to react with the Si—S bond in thiosilanes to yield a variety of linear and cyclic products.

Thus chlorotrimethyltin reacts with isopropylthiotrimethylsilane to yield the corresponding tin compound (6) while 2,2-dimethyl-2-sila-1,3-dithiacyclopentane reacts with both dimethyltin dichloride and stannic chloride (exothermically at room temperature) to yield the stannacyclopentane and the spiran (11).



Hexaethylditin sulfide reacts with both stannous and stannic chlorides to yield the corresponding sulfide (25).

Dissolving hexamethylcyclotritin sulfide in dimethyltin dihalides above their melting points resulted in rapid exchange of the halogen atom with the sulfur bridge. The rate decreases with increasing atomic weight of the halogen (Cl, Br, I) and an NMR study of the iodide case establishes random sorting (155).



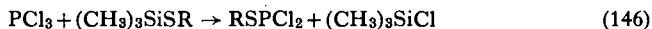
A similar study has been conducted with cyclic silthianes and $(\text{CH}_3)_2\text{SiX}_2$, where X is Cl, OCH_3 , or SCH_3 (155a).

3. Group V

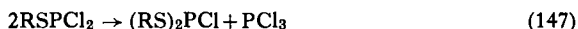
a. *Phosphorus*. A study of the reactions of phosphorus halides with

silicon-sulfur compounds again illustrates the use of the latter as synthetic intermediates (9).

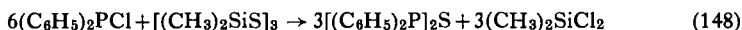
Alkylthiotrimethylsilanes react with phosphorus trichloride and tribromide, phenylphosphorus chlorides, and phosphoryl chloride to yield fully or partially substituted esters of the corresponding thiophosphorus acid, e.g.,



Disproportionation of some of the products has also been shown to occur.



Diphenylphosphorus chloride reacts with hexamethylcyclotrisilthiane to yield tetraphenyl thiophosphinous anhydride.

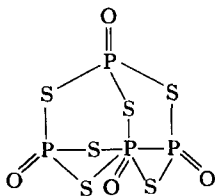
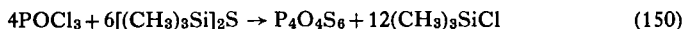


Phenylphosphorus dichloride reacts with silthianes, whether linear or cyclic, to yield the same cyclothiophosphonous anhydride $(\text{C}_6\text{H}_5\text{PS})_3$, e.g.,

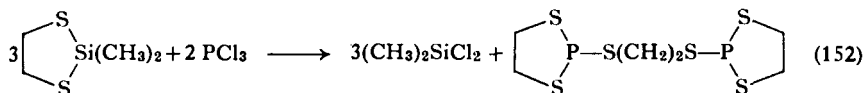
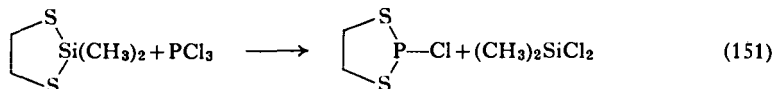


Attempts at preparing a phosphorus sulfide analogous to B_2S_3 from phosphorus trichloride and hexamethyldisilthiane resulted in the formation of a compound whose X-ray photograph resembled the well-known sulfide P_4S_7 , and it is possible that dimerization and disproportionation of P_2S_3 occurred.

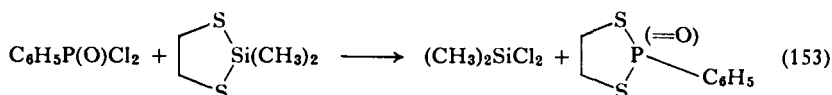
With phosphoryl chloride, however, $\text{P}_4\text{O}_4\text{S}_6$ was successfully isolated and probably has a structure similar to that of P_4O_{10} .



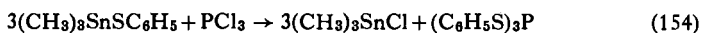
Phosphorus trichloride, like boron trichloride, reacts with 2,2-dimethyl-2-sila-1,3-dithiacyclopentane, to produce two compounds, depending on the proportions used. Thus, the 1:1 reaction yields the simple phosphacyclopentane, but a 2:3 addition results in the formation of what is probably the 1,2-bis(phosphacyclopentylthio)ethane derivative, as indicated by its NMR spectrum (11).



Phenylphosphorus dichloride and phenylphosphoryl dichloride react to produce the corresponding heterocycles.

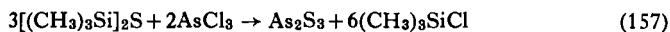
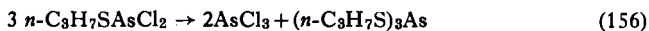
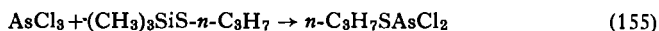


The tin-sulfur bond in phenylthiotrimethyltin is cleaved in a similar way by phosphorus trichloride to yield the trithiophosphite (14).



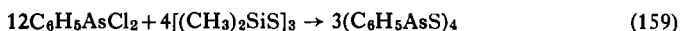
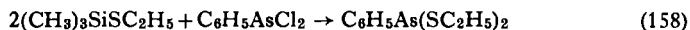
With hexaethylditin sulfide, phosphorus trichloride yielded a mixture of P_4S_{10} and phosphorus, unlike the case of the silthiane, when P_4S_7 resulted (25).

b. *Arsenic*. Arsenic trichloride reacts with both alkylthiosilanes and disilthianes to produce the partially and fully substituted arsines, and arsenic sulfide (5). The alkylthiochloroarsines so produced are even less stable than the corresponding phosphorus compounds, and disproportionate above room temperature into the thioarsenite and arsenic trichloride.



Hexaethylditin sulfide reacts similarly (25).

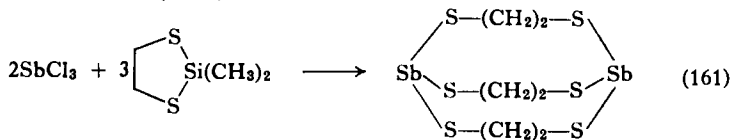
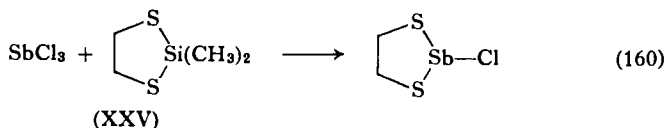
Phenylarsenic dichloride reacts in a similar manner with these two classes of silicon-sulfur compound and with cyclosilthianes to completely replace the halogen atoms (5).



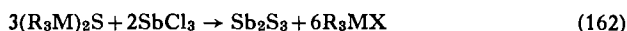
2,2-Dimethyl-2-sila-1,3-dithiacyclopentane reacts with phenylarsenic dichloride to yield the corresponding arsacyclopentane and, as with boron and phosphorus, arsenic trichloride yields two products, the structure of

the fully thiolated one being as previously postulated for boron and phosphorus (11).

c. *Antimony*. The two modes of reaction of the trihalides of boron, phosphorus, and arsenic with 2,2-dimethyl-2-sila-1,3-dithiacyclopentane (XXV) apply equally well to antimony trichloride and resulted in the formation of the silacyclopentane if a 1:1 ratio was used. With the proportions 3:2, however, the product isolated was the "barrel" form indicated, and attempts to prepare the "ring-chain-ring" form isolated for boron, phosphorus, and arsenic by reaction of the chlorostibacyclopentane with (XXV) resulted in the production of polymers (11).

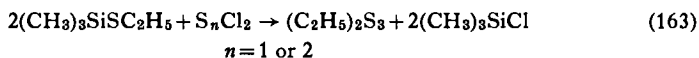


With hexamethyldisilthiane (5) and hexamethylditin sulfide (15), antimony trisulfide was produced on addition of antimony trichloride.



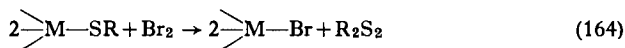
4. Group VI

Apart from the reactions of alkali metal derivatives of the Group IV metal-sulfur compounds with sulfur halides, only the reactions of sulfur dichloride and disulfur dichloride with ethylthiotrimethylsilane have been reported. Diethyl trisulfide was produced in both reactions (4).



5. Group VII

Bromine has been shown to cleave silicon-, germanium- and tin-sulfur bonds, with the formation of disulfides in all cases. Thus, both tris(alkylthio)silanes (257) and *n*-butylthiotrimethylsilane (4) react with bromine to produce the dialkyl disulfides in good yield, while tetra(*p*-tolylthio)-germane (39) and phenylthiotrimethyltin (14) react similarly.



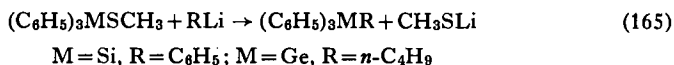
Iodine reacts quantitatively with the tin-sulfur bond, and this has been employed as an analytical procedure for sulfur in tin compounds (14). It has also been shown to oxidize triphenylgermanethiol to the disulfide, $[(C_6H_5)_3GeS]_2$.

The halogens are also reported to cleave the germanium-sulfur bond in the sodium salt of triphenylgermanethiol, but no products were identified (104).

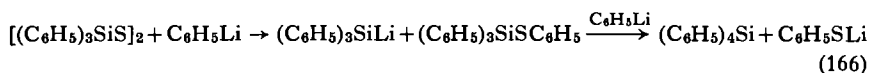
F. Reactions with Organolithium Compounds

The reactions are restricted to sulphur compounds of silicon and germanium.

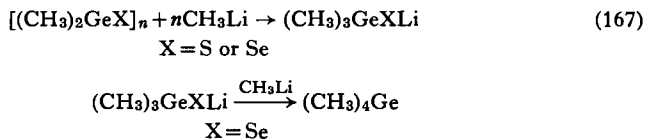
Phenyl lithium has been shown to react with methylthiotriphenylsilane to yield tetraphenylsilane (89), while butyllithium reacts similarly with the analogous germanium compound (107).



Hexaphenyldisilidithiane reacts with two moles of phenyllithium to give similar products, and the initial reaction probably involves cleavage of the S—S bond (46).



Methylolithium has been shown to react with both trimeric dimethylgermanium sulfide and polymeric dimethylgermanium selenide to yield the lithium salt salt of trimethylgermanethiol (189) or selenol (190). With the selenium compound, excess methylolithium yields tetramethylgermane.



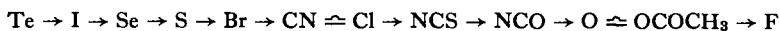
Triphenylsilyllithium has been shown to cleave the Si—S bond in *p*-tolylthiotriphenylsilane to yield hexaphenyldisilane (91, 255).



G. Reactions with Metal Salts

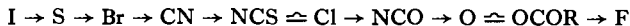
1. Silver

An investigation into the reactivity of Group IV metal-sulfur compounds with various silver salts has led to some interesting reactivity trends, which have been tabulated in the form of a reactivity series. Thus, organosilicon, -germanium, and -tin iodides all react with silver sulfide to produce the organometal sulfide. These sulfides vary in reactivity towards other silver salts. With silicon, reaction with the chloride, bromide, cyanide, isothiocyanate, and isocyanate results in the formation of silver sulfide, while recently, the silyl selenide and telluride have been investigated. The order of reactivity is as indicated (27, 71, 72, 107).

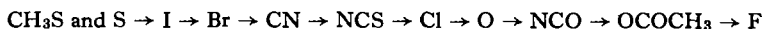


Conversion occurs using the appropriate silver salt on any silicon compound to its left in the series. Reaction will not occur with any other (except where an equilibrium is established).

Similar studies have been made with germanium (23) and tin (28) compounds and the two series listed below established. With germanium, the order differs slightly from silicon

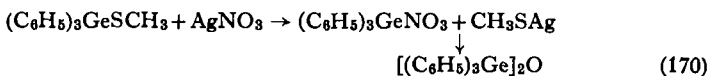
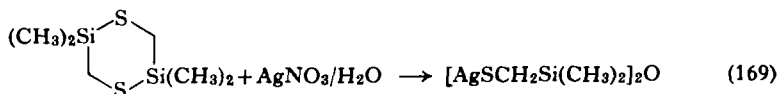


but with tin, further differences arise, notably the order of S and I.



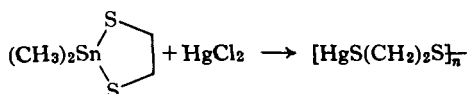
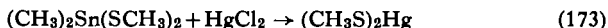
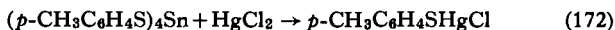
This apparently contradicts the work of Srivastava and Tandon (226), who report that triphenyltin iodide reacts with silver sulfide, though the series was established for ethyl derivatives. Since many factors apart from simple bond energies are concerned in the conversions, such a divergence is not serious.

An aqueous solution of silver nitrate reacts with 1,1,4,4-tetramethyl-1,4-disila-2,5-dithiacyclohexane to yield the silver salt of *sym*-bis(thiomethyl)-tetramethyldisiloxane (211), while with methylthiotriphenylgermane, the germoxane and silver methylmercaptide result (107).

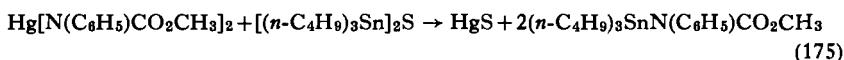


2. Mercury

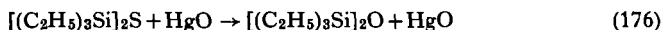
Mercuric chloride is reported to cleave the germanium- and tin-sulfur bonds. With germanium, only the chlorogermane formed was characterized (22) but with tin, the mercury-sulfur compound formed was identified (15, 36).



Hexamethylditin sulfide reacts in a similar way to produce mercuric sulfide, while hexa-*n*-butylditin sulfide and *N*-mercuricarbamates yield this sulfide and the *N*-stannylcarbamate (70).

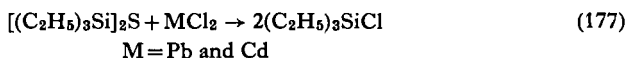


It is convenient to mention here that mercuric oxide will cleave the silicon-sulfur bond in hexaethyldisilthiane with the formation of the sulfide and siloxane (72).



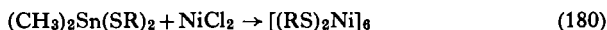
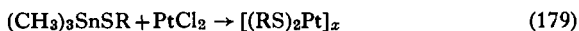
3. Miscellaneous Salts

The dichlorides of lead and cadmium cleave the silicon-sulfur bond in hexaethyldisilthiane to yield chlorotriethylsilane, but the sulfur derivative of the metal was not characterized (72).



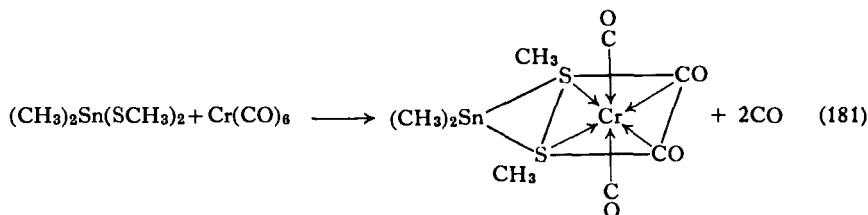
sym-Tetramethyldisilthiane reacts with titanium tetrachloride and palladous chloride to produce a variety of products (80). The former reacts not only with the Si—S bond, but breaks the Si—H one, to produce dichlorodimethylsilane. With palladous chloride, some hydrogen and hydrogen sulfide was isolated. Cuprous chloride did not react.

Organotin-sulfur compounds react with chlorides of cadmium, platinum, and nickel as indicated (15)

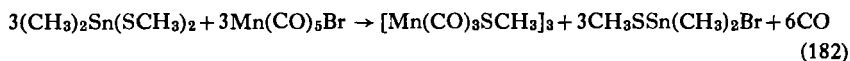


Despite the use of excess of the tin-sulfur compound with cadmium chloride, only one chlorine atom reacted, but the use of platinum and nickel chlorides resulted in complete replacement and yielded polymeric mercaptides.

The reaction of bis(methylthio)dimethyltin with chromium carbonyl results in the formation of a chelated complex (17).



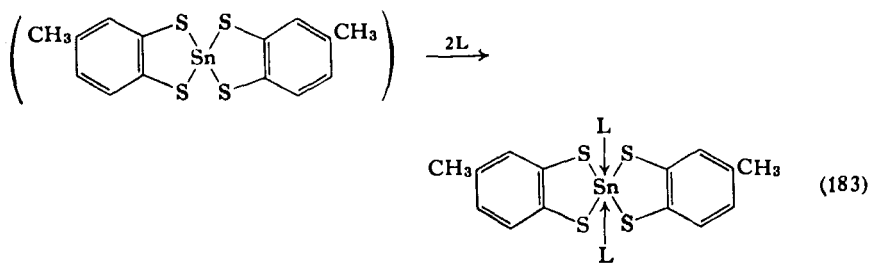
With manganese pentacarbonyl bromide, however, cleavage of the metal-bromine bond also occurs, yielding an alkylthiocarbonyl complex $[\text{Mn}(\text{CO})_3\text{SR}]_3$ (18).



H. Miscellaneous Reactions

1. Coordination of the Group IV Metal-Sulfur Compounds

Attempts to form a simple adduct of *sym*-tetramethyldisilthiane with boron trimethyl indicated no reaction (78). However, coordination to tin-sulfur compounds appears to be well established (175). The lithium salt of triphenyltin thiol is dimeric (216) while the tin-sulfur compound derived from stannic chloride and toluene-3,4-dithiol is polymeric. This polymer can be broken down by alkali and organic bases (175).

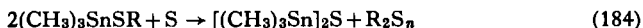


$\text{L} = \text{OH}^-$, pyridine, or dimethylformamide

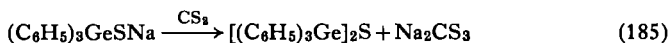
The organic ligand is lost on heating and this polymeric tin complex has been used as a colorimetric (175) and photometric (65) agent for identifying tin.

2. Sulfur and Sulfur-Containing Compounds

Attempts to add sulfur across the tin-sulfur bond in alkylthiotin compounds resulted only in the isolation of hexamethylditin sulfide and organic polysulfides (14).



Carbon disulfide treated with the sodium salt of triphenylgermanethiol and methyl iodide did not produce the expected methyltriphenylgermylthiocarbonate. Hexaphenyldigermthiane and sodium trithiocarbonate were the only isolated products (105).



No multiple bond addition occurred in acrylonitrile using triphenylgermanethiol, but with thiocyanogen, the germyl thiocyanate was formed, together with sulfur (104).



IV

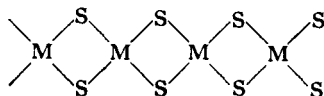
PHYSICAL PROPERTIES

Considering the many and varied classes of the Group IV metal-sulfur compounds that have been synthesized, and their industrial uses, it is surprising that so little work has been devoted to determining their physical properties. In the light of this, we have reviewed the field by considering the physical technique employed and the information so derived. Consequently, it will be possible to see which techniques prove most fruitful and where further work could most profitably be conducted.

A. X-Ray Diffraction

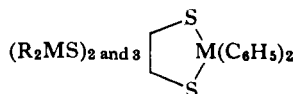
Although this is the most definitive method for obtaining structural information, no molecular parameters of organo Group IV metal-sulfur compounds have been obtained. The unit cell dimensions of tetraorgano thio and seleno derivatives of silicon, germanium, and tin have been deter-

mined (33, 34, 40, 117–119) but only in the cases of silicon and germanium disulfides have bond lengths and angles been estimated. Both disulfides are polymeric, involving chains of four membered rings.



With silicon disulfide, the Si—S bond length was found to be 2.14 Å (263), with angles of 100° and 80° at silicon and sulphur (60), indicating planarity. The data obtained for germanium disulfide includes a Ge—S bond length of 2.19 Å (262) and a S—Ge—S angle of 103°.

It would be most worthwhile to investigate the structures of some of the solids reviewed here, especially among the cyclic compounds, e.g.,



and the spiro compounds.

B. Electron and Neutron Diffraction

Structural information for several silicon–sulfur compounds has been obtained using electron diffraction techniques, and is summarized in Table I.

TABLE I
DATA OBTAINED BY ELECTRON DIFFRACTION

Compound	Si—S bond length (Å)	Si—S—Si	S—Si—S	Structure	Reference
$[(\text{CH}_3)_2\text{SiS}]_2$	2.18 ± 0.03	75°	105°	Planar	260, 261
$[(\text{CH}_3)_2\text{SiS}]_3$	2.15 ± 0.03	110°	115°	Puckered	260, 261
Cl_3SiSH	2.14 ± 0.02	—	—	—	253
$(\text{H}_3\text{Si})_2\text{S}$	2.136 ± 0.002	$97.4 \pm 0.7^\circ$	—	—	20

Values agree well with those obtained by X-ray techniques.

No neutron diffraction work has been reported to date, and the only microwave spectroscopy mentioned on Group IV sulfur compounds concerns dimethyl sulfide. The observed C—S bond length was 1.802 ± 0.002 Å while a C—S—C angle of $98^\circ 52'$ was obtained (169). This tends to support lack of π bonding in disilyl sulfide, where the Si—S—Si angle is 97° (20), though σ -bonding hybrid orbitals involving the sulfur d orbitals will keep the value of the angle low while still permitting π bonding to occur.

The Si—S—Si angle of 75° does not in fact measure the angle between the bonding electron pairs. These have been shown to contain a slightly greater angle and so the bonds are slightly bent (87). This may explain the slightly longer bonds reported in $(\text{Me}_2\text{SiS})_2$ compared with other silicon-sulfur compounds.

C. Infrared and Raman Spectroscopy

The spectroscopic data available on the Group IV metal-sulfur compounds will be considered in two sections, the first involving structural interpretations from the spectra, and the second, group frequencies of the various vibrating systems.

1. Structural Interpretations

Kriegsmann (131) has shown that the infrared and raman spectra of tetramethylcyclodisilthiane are consistent with a planar structure of D_{2h} symmetry, and that hexamethylcyclotrisilthiane probably occurs in the boat form with C_s symmetry, with a Si—S—Si angle of 104° and bond energy and force constant for the Si—S bond of 64 kcal and 2.2 mdyne/Å (130). The Si—S bond in trimethylsilanethiol also has a force constant of 2.20 mdyne/Å (128, 129), which has been interpreted as indicating a bond order of 1.0 (94).

Disilyl sulfide and selenide and their deuterated analogs are all shown to be bent, the sulfur compounds possessing a Si—S—Si angle of about 100° (75, 145).

The Raman spectrum of tetrachlorocyclodisilthiane is consistent with a planar structure and the Si—S force constant of 2.28 mdyne/Å tends to suggest partial double bonding (95).

Digermyl ether and sulfide are both bent, and this is reported as indicating a decrease in the use of the d orbitals as compared with silicon (93).

2. Group Frequencies

The vibrational frequencies reported for Group IV metal-sulfur compounds will be listed under their respective elements.

a. *Silicon*. The Si—S—Si grouping is reported to have symmetrical and antisymmetrical stretching frequencies (ν_s and ν_{as}) at 438 and 489 cm^{-1} (107, 130, 131, 210) for linear and cyclic silthianes of the types reported in the Appendix of compounds. Disilthiane, however, has these vibrations at higher frequencies (480, 517 cm^{-1}) (75) as does compound XIX (445, 529 cm^{-1}) (237).

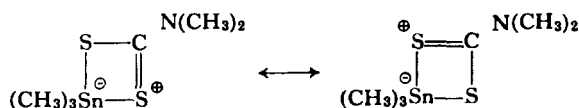
For the Si—S—C group ν_s and ν_{as} are reported over a wide frequency range, depending on other groups bonded. Thus ν_s is reported from 640 to 512 cm^{-1} with ν_{as} , 520 to 486 cm^{-1} (2, 107).

Tetraphenylcyclodisilthiane and hexaphenylcyclotrisilthiane have typical vibrational frequencies at 744 cm^{-1} and 733 cm^{-1} (154) while the Si—Se bond has a stretching frequency at 390 cm^{-1} in disilyl selenide (75).

b. *Germanium*. For the Ge—S—Ge group ν_s and ν_{as} are reported at 385 and 411–417 cm^{-1} , while those of Ge—S—C are at 400 and 404 cm^{-1} (57, 214).

c. *Tin*. For the Sn—S—Sn group ν_s and ν_{as} occur at 330 and 376 cm^{-1} (214) while the two stretching frequencies of Sn—S—C are found at 355–361 and 365–368 cm^{-1} (214).

The carbon disulfide adduct with dimethylaminotrimethyltin, $(\text{CH}_3)_3\text{SnSC}(\text{S})\text{N}(\text{CH}_3)_2$, has two peaks at 448 and 507 cm^{-1} attributed to ν_s and ν_{as} for the S—Sn—S group, formed by intramolecular coordination (85).



The far-infrared spectra of various tin-sulfur and tin-selenium compounds are also reported (132).

d. *Lead*. For the Pb—S—Pb group ν_s and ν_{as} are reported at 278 and 336 cm^{-1} (214) while the vibrations for Pb—S—C occur at 303 and 305 cm^{-1} .

D. Nuclear Magnetic Resonance Spectroscopy

An examination of the NMR spectra of various silyl compounds shows that a plot of the coupling constant J_{HH} against $J_{\text{Si}^*\text{H}}$ gives a straight line

plot for Cl, Br, I, S, and H together with a parallel plot for the fluoride, amine, and oxide. It is tempting to associate this difference with the ease of π bonding associated with silicon and the donor elements of the first period, but the possibility of hyperconjugative explanations arise (76).

This π -bonding theory has been used as an explanation for the trends associated with the trimethylsilyl analogs of the above compounds. Thus an increase in the deshielding of protons in the series $[(\text{CH}_3)_3\text{Si}]_2\text{X}$ ($\text{X} = \text{O}, \text{S}, \text{Se}$) is observed, together with the corresponding increase in J_{HC^*} and J_{HCSi^*} (201). These results contradict electronegativity trends and are interpreted in terms of a decrease in π bonding from the donor element as the atomic weight increases. This will induce an increase in s character on silicon and carbon and consequently increase the J values.

A comparison of the various δ and J values for the series $(\text{CH}_3)_3\text{SiSM}(\text{CH}_3)_3$ ($\text{M} = \text{Si}, \text{Ge}$ and Sn) and $[(\text{CH}_3)_3\text{M}]_2\text{S}$ shows that $\delta[(\text{CH}_3)_3\text{Si}]$ moves to higher fields as the atomic weight of M increases, indicating an increase in π bonding to Si with M . J values vary little, however, compared with analogous oxygen compounds, where π bonding is much stronger.

Values of $\delta_{\text{M}(\text{CH}_3)_3}$ ($\text{M} = \text{Ge}, \text{Sn}$) are less than the values reported for $[(\text{CH}_3)_3\text{M}]_2\text{S}$ as would be expected, while an increase in J_{HC^*} of $(\text{CH}_3)_3\text{M}$ occurs with the increase expected in s character of M . However, they do not differ significantly from J for $[(\text{CH}_3)_3\text{M}]_2\text{S}$.

A comparison of $[(\text{CH}_3)_3\text{M}]_2\text{X}$ for $\text{M} = \text{Ge}, \text{Sn}$; $\text{X} = \text{O}, \text{S}, \text{Se}$ again shows an increase in $|\delta|$ which contradicts electronegativity trends. As π bonding is considered weak for Ge and Sn compounds, it seems that some other explanation is required to interpret these trends (202).

1. Group Frequencies

There is much PMR spectral data for compounds of the Group IV and VI elements, and information is given in the references quoted: *silicon-sulfur* (107, 155a, 237, 246-249); *germanium-sulfur* (107, 189, 247-250); *germanium-selenium* (190); *tin-sulfur* (155, 189, 247-249); *tin-selenium* (190).

E. Dipole Moments

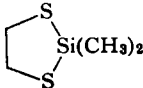
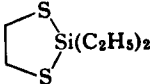
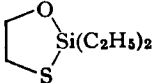
No dipole moment determinations have been made directly on organo Group IV metal-sulfur compounds but if the atomic polarization of hexa-

methylcyclotrisilthiane is assumed to be approximately the same as the oxygen analog, then a dipole moment of 1.03 D can be determined. The dipole moment of tetramethylcyclodisilthiane was found similarly and shown to be zero, indicating a planar structure with an atomic polarization of 9.0 cc. (139).

F. Bond Parachors

Agreement between the experimental and calculated parachor for disilyl sulfide can only be obtained if the "polar" Si—H parachor is used in the calculation (152). This is obtained from silyl compounds in which partial double bonding is known to occur (e.g., silyl fluoride or disiloxane), thereby implying a certain degree of double bonding between silicon and sulfur.

TABLE II
MOLAR REFRACTIVITIES

Compound	Refractivity	Reference
$(\text{CH}_3)_3\text{SiCH}_2\text{Si}(\text{CH}_3)_2\text{SH}$	56.53	234
$[(\text{CH}_3)_3\text{SiCH}_2\text{Si}(\text{CH}_3)_2]_2\text{S}$	103.84	234
$(\text{C}_2\text{H}_5)_3\text{SiCH}_2\text{Si}(\text{C}_2\text{H}_5)_2\text{SH}$	79.24	234
$[(\text{C}_2\text{H}_5)_3\text{SiCH}_2\text{Si}(\text{C}_2\text{H}_5)_2]_2\text{S}$	149.00	234
$(\text{CH}_3)_3\text{SiSP}(\text{S})(\text{OC}_2\text{H}_5)_2$	71.27	84
$(\text{CH}_3)_3\text{SiSP}(\text{S})(\text{OCH}_3)_2$	62.04	84
	43.65	P55
	53.15	P55
	36.24	P55

G. Magnetic Susceptibility

Very little work has been conducted on the diamagnetic susceptibility of Group IV metal-sulfur compounds. Values for the molecular susceptibilities of tetraphenylthiogermane (166) and several series of tin-sulfur compounds (16) have been determined, the latter giving anomalously low values for the atomic susceptibility of tin, due possibly to $p\pi-d\pi$ bonding from sulfur.

H. Molar Refractivities

Values for the molar refractivities of the compounds listed in Table II have been determined but no interpretations made.

The tin-sulfur bond refractivity is reported as 7.631 (197). Vapor-phase chromatography retention data have been determined for several silicon-sulfur compounds (173).

V

THEORETICAL CONSIDERATIONS

In this section, the nature of the Group IV metal-sulfur bond will be discussed in the light of the chemical and physical properties already surveyed. Factors influencing the nature of these bonds when considered in isolation can be discussed under three headings, namely, bond strength, the electronegativity of the Group IV elements, and the possibility of π bonding between sulfur and the Group IV element. Inevitably, however, all these factors influence the nature of the bond at the same time.

A. Bond Strength

Very little has been determined for the Group IV metal-sulfur bonds and trends can best be seen from the synthetic and chemical properties sections already reviewed.

The shortening of bonds whose length is found to be less than the value predicted from the sum of covalent radii can be attributed to two effects. The first is ionic and arises because of the difference of electronegativities of the two elements. This results in a distortion of the charge cloud with

resultant shortening. The second effect is π bonding, which occurs between filled nonbonding orbitals on one atom forming a dative π bond with empty orbitals on the other, assuming the orbital energies and symmetry tally (239).

B. Electronegativity

This is one of those nebulous terms in chemistry that has to be used carefully, for while appearing quantitatively satisfactory in one situation it may be qualitatively in error in another. As a result of this there are two trends in the electronegativities of the Group IV elements currently under consideration. A steady increase in the electropositive nature of the Group IV element with atomic weight is proposed (167, 176), while alternating electronegativity values are also considered (19, 192). A brief summary of their limitations is given by Rijkens and van der Kerk (185), who point out that bond polarity is of much more importance, and depends not only on electronegativity, but also on the bonding between elements concerned.

C. π Bonding in Silicon Compounds

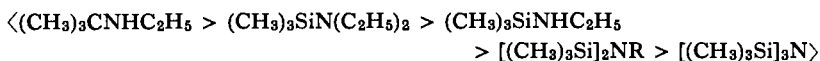
Before considering the possibility of π bonding from sulfur to the Group IV elements, it is probably advisable to discuss π bonding from nitrogen

TABLE III
EFFECTS OF π BONDING

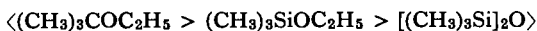
	Si—N		Si—O	
	Found	Theory	Found	Theory
Bond length (Å)	1.74 ± 0.02 (74) 1.72 ± 0.03 (187)	1.81 (74)	1.63 ± 0.04 (74) 1.69 ± 0.03 (74)	1.76 (74)
Force constant (mdyn Å)	4.1 (74)	3.3 (74)	4.7	3.7 (74)
Bond angle for				
Si—M—C	$130 \pm 5^\circ$ (187)	$109^\circ 28'$	$130 \pm 10^\circ$ (74)	$109^\circ 28'$
Si—M—Si	$119.6 \pm 1^\circ$ (74) 131° (130)	$109^\circ 28'$	$130 \pm 10^\circ$ (139) 145° (74)	$109^\circ 28'$

and oxygen to silicon and the way such bonding, which is now well established (73, 74), influences both the physical and chemical properties of the compounds concerned. Table III gives a list of data for silicon-oxygen and silicon-nitrogen compounds, together with values predicted for the absence of π bonding, when the electronegativity difference corrections have been applied (212).

Not only does this π bonding influence the physical properties of the compounds, but, naturally it has an effect on their chemical properties. The obvious influence is on their basicity. Thus methoxysilane is reported not to form an adduct with diborane (227), and trisilylamine and *N*-methyl-disilazane are only weakly basic compared with trimethylamine (74). A true comparison of the basicity of these compounds is difficult since they often undergo fission with the conventional acids, such as hydrogen chloride or the boron halides. The use of protonated materials such as alcohols and amines (241), and spectroscopic techniques have led to advances in our knowledge of the factors influencing the basicity of these compounds, and comparisons have been done using deuteriochloroform as the reference acid (13). Variations in the C—D stretching frequency in the infrared spectrum of deuteriochloroform in mixtures with various bases as measured from the value in the vapor phase have been used to show relative orders of basicity indicated in the two series below.



and



Here, the differences in electronegativity of silicon and carbon and their influence on donor ability is completely over-ruled by the π bonding from nitrogen and oxygen to silicon and the greater the number of silicon atoms around the donor, the weaker becomes the base. This reduction in basicity shows up in the lack of complexing with boron compounds (78).

With germanium, tin, and lead, the π bonding decreases with increase in atomic weight, with an increased tendency for intermolecular bonding and polymerization. Thus methoxytrimethylgermane yields a 1:1 adduct with BF_3 which sublimates at 25°C (185), and trimethyltin hydroxide (133) and $(\text{R}_2\text{SnX})_2\text{O}$ (164) are dimeric, with bridging oxygen atoms. Also, siloxy derivatives of the Group IV elements $(\text{R}_3\text{SiO})_n\text{MR}_{4-n}$ and $(\text{CH}_3)_3\text{-SiOM}(\text{CH}_3)_3$ show an increase in polarity of the M—O bond with $\text{M} = \text{Si} \rightarrow \text{Pb}$, due to a decrease in electronegativity and π bonding (185).

The infrared spectra of $[(\text{CH}_3)_3\text{Si}]_2\text{NMR}_3$ compounds show a decrease in π bonding with increase in atomic weight of M. This also shows in the properties of the triphenyl azides of the Group IV elements (185).

D. The Group IV Metal-Sulfur Compounds

Estimated bond lengths and force constants for the M—S bond in some of these compounds have been determined (Table IV).

TABLE IV
DATA ON GROUP IV METAL-SULFUR COMPOUNDS

	Bond length (Å)		Force constant		References
	Observed	Calculated	Observed	Calculated	
C—S	1.802 ± 0.002	1.81	3.3	3.2	(225)
Si—S	2.14 ± 0.02	2.15	2.2	2.2	(167)
Ge—S	2.19	2.23	—	—	(262, 167)
Sn—S	—	2.43	—	—	(167)

From the evidence to date the physical properties of silicon-sulfur compounds tend to indicate a lack of multiple bonding, with the bond length, force constant, and bond angles all supporting sp^3 -hybridized silicon and sulfur. However, the high force constant for the silicon-sulfur bond in $(\text{Cl}_2\text{SiS})_2$ does tend to indicate π bonding as predicted (229), and may well be due to the presence of the electronegative chlorine atoms. Also, the lack of coordination of silyl sulfides tends to support the π bonding theory (78). Dialkyl sulfides coordinate extensively with boron compounds, but silyl analogs would be expected to be stronger bases on electronegativity grounds.

There is little physical data available for organogermanium-, tin-, and lead-sulfur compounds. That for germanium indicates little or no π bonding, while the polymeric nature of some tin-sulfur compounds (175) tends to

support this. Thus any tendency to increase the coordination number is done externally rather than internally.

An examination of the donor ability of Group IV metal-sulfur compounds in a manner analogous to that for Si—N ones gives results in Table V (7).

TABLE V
FREQUENCY SHIFTS OF BASE/ CDCl_3 MIXTURES FOR ν_{CD} FROM ν_{CD} VAPOR

M	Series		
	$(\text{CH}_3)_3\text{MSCH}_3$	$(\text{CH}_3)_3\text{MSC}_2\text{H}_5$	$[(\text{CH}_3)_3\text{M}]_2\text{S}$
C	33	36	40
Si	29	32	29
Ge	34	36	38
Sn	36	41	43
Pb	49	53	51

The varying electronegativities of the elements would lead to silicon, germanium, and tin being the strongest bases, followed by lead and carbon. It is doubtful whether the small differences in electronegativity between Si, Ge, and Sn compounds would have as pronounced an effect on the donor ability as shown in the three series. So it seems probable that π bonding plays some role, certainly in the case of silicon and germanium compounds, which are all either weaker or the same strength as their isostructural carbon analogs. This effect may be negligible with tin but the large increase in donor ability of the lead compounds, despite electronegativity increase, tends to indicate other factors influencing the basicity; $d\pi-d\pi$ bonding may occur from the filled lead d orbitals into the vacant sulfur ones.

A similar study using variations in the proton shift of CHCl_3 in the NMR spectrum indicates similar trends but here, steric factors influence the signal's position as well as electronic ones, and therefore care has to be taken in interpreting them (12). However, determinations at various temperatures leads to the evaluation of the heat of formation of these hydrogen bonds.

VI

INDUSTRIAL INTERESTS

At the end of this review are listed 111 references to the patent literature which contain mention of compounds pertinent to this article. No claim is made that this is an exhaustive list, but it does serve to indicate the industrial interest in these materials. The patent references have been kept separate and prefixed *P*, in order that in the text and tables, it will be immediately obvious to the reader whether a reference is a patent or otherwise.

A. Silicon and Germanium

Despite the now very extensive use of organosilicon compounds on an industrial scale there appears to be very little known of commercial applications of the sulfur compounds. Organosilicon-sulfur compounds have been mentioned in the following contexts: heat stabilizers and antifoam agents in mineral oils (*P55*) and lubricants (*P59*), additives to silicones, fungicides and insecticides (*P54*), and as possible promoters to dropwise condensation of steam (*47, 48*). A few germanium-sulfur compounds have been used in an effort to treat infections in mice, but have proved valueless (*188*). Their toxicity depended on structure, but was much less than that of similar tin and lead compounds.

B. Tin

Organotin-sulfur compounds are now manufactured commercially on a large and ever increasing scale. They possess good thermal stability (*P106*) and the major outlet for these compounds is as stabilizers for polyvinyl chloride and related plastic materials (*P6, P19, P26, P31, P32, P37, P38, P66, P68, P72, P84, P86, P87, P93, P104, P107, P110*). Organotin compounds have been used as stabilizers since the 1930's (*P52*), but only in 1950 (*P5, P69*) was the first report made of superior stabilizers containing the tin-sulfur linkage. Compounds of this first claim had the general formula $R_2Sn(SR')_2$. Three days later compounds of general formulas R_3SnSR' , $R_2Sn(SR')_2$, $RSn(SR')_3$, and $Sn(SR')_4$ were all claimed by a different research team to have stabilization properties! Subsequent variations in the structures of compounds containing tin-sulfur bonds for use

(110, 116) as PVC stabilizers have been boundless, particularly in the fields of mercapto acids (*P26, P31*) and mercapto esters (*P8–P10, P15, P16, P56, P73, P93, P107*). One major producer of organotin compounds now reports that over 90% of their production is of organotin–sulfur compounds. An eminently readable account of the development of these compounds has been compiled by Verity-Smith (235). A large number of the compounds which appear in the tables at the end of this article have been extracted from patents claiming their synthesis or utilization. In many cases, however, it will be noted that no characterization of the product was offered.

In addition to the stabilization of vinyl polymers, tin–sulfur compounds have been claimed as stabilizers of polythene (*P23, P25, P46, P92*) and as rubber curing agents (*P85, P89*).

Other uses (112) noted for organotin–sulfur derivations are as lubricant additives (*31, P22, P34, P51, P74, P95*), acaricides (*P29*), grain and plant fungicides (*P44, P105*), general fungicides, insecticides and bactericides (*51, P27, P43, P48, P108, P109*), controller of armyworm, cotton leaf perforator, and bean aphids (*P101*), and for the production of nontacky urethane foams (*P46, P49*).

C. Lead

Compared with tin, little industrial interest appears to attach to organo-lead–sulfur compounds. $(\text{CH}_3)_3\text{PbSCH}_3$ (*P97*), $\text{R}_3\text{PbSCH}_2\text{CONH}_2$ (*P99*), and $[(\text{CH}_3)_3\text{Pb}]_2\text{S}$ (*P96*) have been mentioned as potential motor engine antidetonants, and the $\text{R}_3\text{PbSCH}_2\text{CONH}_2$ types (*P99*) are claimed as potential pesticides.

VII

APPENDIX: TABULAR SURVEY

TABLE 1
COMPOUNDS OF GENERAL FORMULA R_3MSR'

Compound	M.p. (°C)	B.p. (°C)/mm	d_D^{20}	n_D^{20}	References
<i>Silicon</i>					
$(CH_3)_2Si(OC_2H_5)SC(S)N(C_2H_5)_2$					54
$(CH_3)_2Si(Cl)SC_2H_5$	145°			1.4662	4
$(CH_3)_3SiSCH_3$	110°–111°		0.832	1.4484 (23°)	6, 107
$(CH_3)_3SiSC(S)N(CH_3)_2$	98°–105°/1–2.5			1.5640	54, 55
$(CH_3)_3SiSC(S)N(C_2H_5)_2$	92°–97°/0.7			1.5481	54, 55
$(CH_3)_3SiSC_2H_5$	130°	0.832		1.4512	2
$(CH_3)_3SiSC_3H_5$	150°/740				P71
$(CH_3)_3SiS-n-C_3H_7$	151°	0.844		1.4524	2
$(CH_3)_3SiS-iso-C_3H_7$	142°	0.824		1.4497	2
$(CH_3)_3SiS-n-C_4H_9$	168°	0.854		1.4550	2, 115, 140
	76°–77°/40				
$(CH_3)_3SiS-tert-C_4H_9$	157°	0.834		1.4570	2
$(CH_3)_3SiS-n-C_{12}H_{25}$	210°–215°/0.1			1.4750	47, 48
$(CH_3)_3SiSC_6H_5$	40°/0.3	0.890		1.5560	107
$(CH_3)_3SiSP(S)(OCH_3)_2$	44°–46°/0.001	1.119		1.5148	84
$(CH_3)_3SiSP(S)(OC_2H_5)_2$	55°–56°/0.001	1.084		1.5098	44, 84
$(C_2H_5)_3SiSC_2H_5$	56°–58°/0.1				1, 99
$(n-C_3H_7)_3SiSC_6H_5$	149°–150°/10				P111

TABLE 1—Continued

Compound	M.p. (°C)	B.p. (°C)/mm	d_D^{20}	n_D^{20}	References
<i>Silicon</i> (continued)					
(<i>n</i> -C ₄ H ₉) ₃ SiS- <i>n</i> -C ₄ H ₉					210
(C ₆ H ₅) ₃ SiSCH ₃	83°–84°	145°–150°/0.06 148°–156°/0.04			46, 89
(C ₆ H ₅) ₃ SiSC ₂ H ₅	87°–88°	155°–162°/0.04			46
(C ₆ H ₅) ₃ SiS- <i>n</i> -C ₃ H ₅	73°–74°	166°–173°/0.03			46
(C ₆ H ₅) ₃ SiS- <i>n</i> -C ₃ H ₇	70°–71°	162°–172°/0.04			46
(C ₆ H ₅) ₃ SiS-iso-C ₃ H ₇	84°	157°–162°/0.03			46
(C ₆ H ₅) ₃ SiSCH ₂ C ₆ H ₅	92°–94°	172°–177°/0.015			89
(C ₆ H ₅) ₃ SiSCOC ₆ H ₅	128°–129°	183°–189°/0.01			89
(C ₆ H ₅) ₃ SiSC(C ₆ H ₅) ₃	169°–170°				46
(C ₆ H ₅) ₃ SiSC ₆ H ₅					46, 256
(C ₆ H ₅) ₃ SiSC ₆ H ₄ CH ₃ - <i>p</i>	79°–80°	250°–265°/3			255
(<i>o</i> -CH ₃ C ₆ H ₄) ₃ SiSC ₆ H ₄ CH ₃ - <i>p</i>	112°–113°				90
<i>Germanium</i>					
(CH ₃) ₃ GeSCH ₃		129°–131°			107
(CH ₃) ₃ GeSC ₂ H ₅		148°	1.10	1.4788 (21°)	6
(CH ₃) ₃ GeS- <i>n</i> -C ₄ H ₉		62°/8	1.08	1.4736 (22°)	6
(CH ₃) ₃ GeS- <i>tert</i> -C ₄ H ₉		25°–26°/0.1	1.08	1.4729 (22°)	6
(CH ₃) ₃ GeSC ₆ H ₅		37°/0.001	1.20	1.5560 (23°)	6
(C ₂ H ₅) ₃ GeSC ₂ H ₅					26
(C ₂ H ₅) ₃ GeSCH ₂ CO ₂ Ge(C ₂ H ₅) ₃		326° 158.5°–159.5°/4	1.2224	1.4993	21, 22
(C ₂ H ₅) ₃ GeS- <i>n</i> -C ₄ H ₉		120°/14	1.0546	1.4880	143
(C ₂ H ₅) ₃ GeS- <i>n</i> -C ₆ H ₁₃		277° 108°–109°/1	1.029	1.488	26

$(\text{C}_2\text{H}_5)_3\text{GeS}-n\text{-C}_7\text{H}_{15}$	288° 117°–118°/1	1.019	1.489	26
$(\text{C}_2\text{H}_5)_3\text{GeS}-n\text{-C}_{12}\text{H}_{25}$	357° 184°–186°/1	0.975	1.481	26
$(\text{C}_2\text{H}_5)_3\text{GeSCH}_2\text{C}_4\text{H}_9\text{O}$	276° (sl. dec) 130°–132°/1	1.177	1.523	26
$(\text{C}_2\text{H}_5)_3\text{GeSCH}_2\text{C}_6\text{H}_5$	305° 130°–131°/1	1.139	1.549	26
$(\text{C}_2\text{H}_5)_3\text{GeSC}_6\text{H}_5$	286° 112°–113°/1	1.153	1.553	26
$(\text{C}_2\text{H}_5)_3\text{GeSC}_6\text{H}_4\text{CH}_3\text{-}o$	298° 123°–124°/1	1.141	1.553	26
$(\text{C}_2\text{H}_5)_3\text{GeSC}_6\text{H}_4\text{CH}_3\text{-}m$	300° 143°–145°/1	1.131	1.550	26
$(\text{C}_2\text{H}_5)_3\text{GeSC}_{10}\text{H}_7\text{-}\beta$	367° (sl. dec) 195°–197°/1	1.184	1.613	26
$(\text{C}_2\text{H}_5)_3\text{GeSC}_6\text{H}_4\text{NH}_2\text{-}o$	326° 163°–164°/1	1.197	1.583	26
$(\text{C}_6\text{H}_5)_3\text{GeSCH}_3$	84°–85° 87°–88°			105, 107
$(\text{C}_6\text{H}_5)_3\text{GeSC}_3\text{H}_5$	62°			69
$(\text{C}_6\text{H}_5)_3\text{GeS}-n\text{-C}_4\text{H}_9$	147°–150°/0.5		1.6135	105
$(\text{C}_6\text{H}_5)_3\text{GeS}-n\text{-C}_{11}\text{H}_{23}$	56°			69
$(\text{C}_6\text{H}_5)_3\text{GeSCH}_2\text{SCH}_3$	63°			105
$(\text{C}_6\text{H}_5)_3\text{GeSCH}_2\text{CONH}_2$	151°			69
$(\text{C}_6\text{H}_5)_3\text{GeSCH}_2\text{CO}_2\text{H}$	149°–150°			69
$(\text{C}_6\text{H}_5)_3\text{GeSCH}_2\text{CO}_2\text{CH}_3$	44°–45°			69
$(\text{C}_6\text{H}_5)_3\text{GeS}(\text{CH}_2)_2\text{OH}$	Oil			69
$(\text{C}_6\text{H}_5)_3\text{GeSCH}_2\text{C}_6\text{H}_5$	98.5°			105
$(\text{C}_6\text{H}_5)_3\text{GeSCOCH}_3$	105°			69

TABLE 1—*Continued*

Compound	M.p. (°C)	B.p. (°C)/mm	d_D^{20}	n_D^{20}	References
<i>Germanium</i> (continued)					
(C ₆ H ₅) ₃ GeSCOC ₆ H ₅	142°–143° 145.5°				105, 219
(C ₆ H ₅) ₃ GeSC ₆ H ₅	90.5°–91.5° 96°				69, 107
(C ₆ H ₅) ₃ GeSC ₆ F ₅	96°–97°				69
(C ₆ H ₅) ₃ GeSC ₆ H ₄ Cl- <i>p</i>	101°–102°				69
(C ₆ H ₅) ₃ GeSC ₁₀ H ₇ - β	88°–89°				69
(C ₆ H ₅) ₃ GeS-17- β -mercaptotestosterone	188°				69
(C ₆ H ₅) ₃ GeSSO ₂ CH ₃					104
(C ₆ H ₅) ₃ GeSSO ₂ C ₆ H ₄ CH ₃ - <i>p</i>					104
<i>Tin</i>					
(CH ₃) ₃ SnSCH ₃	163°		1.453	1.5303	14
(CH ₃) ₃ SnSC ₂ H ₅	177°		1.394	1.5205	14, 66
(CH ₃) ₃ SnS- <i>n</i> -C ₃ H ₇	53°/3		1.352	1.5178	14
(CH ₃) ₃ SnS- <i>iso</i> -C ₃ H ₇	182°		1.318	1.5123	14
(CH ₃) ₃ SnS- <i>n</i> -C ₄ H ₉	44°/0.05		1.281	1.5093	14
(CH ₃) ₃ SnS- <i>tert</i> -C ₄ H ₉	42°/0.1		1.267	1.5083	14
(CH ₃) ₃ SnS- <i>n</i> -C ₈ H ₁₇	94°/0.1		1.175	1.5000	14
(CH ₃) ₃ SnSC ₆ H ₅	69°/0.01		1.418	1.5934	6
(CH ₃) ₃ SnSC ₆ F ₅	62°/0.001		1.71	1.5244	6
(CH ₃) ₃ SnSC(S)N(CH ₃) ₂					85, 113
(C ₂ H ₅) ₃ SnSCH ₃	94°/2 224°		1.375 1.319	1.5274 1.5290	14, 28

$(\text{C}_2\text{H}_5)_3\text{SnSC}_2\text{H}_5$	68°/0.7 125°/12 240°	1.359 1.278	1.5153 1.5150	14, 193
$(\text{C}_2\text{H}_5)_3\text{SnS-iso-C}_3\text{H}_7$	78°–80°/1 256°	1.236	1.5132	193, 195
$(\text{C}_2\text{H}_5)_3\text{SnS-}n\text{-C}_4\text{H}_9$	88°–91°/1 248° (dec)	1.234	1.5133	193
$(\text{C}_2\text{H}_5)_3\text{SnS-iso-C}_4\text{H}_9$	86°–88°/1 243° (dec)		1.5122	193, 195
$(\text{C}_2\text{H}_5)_3\text{SnS-}tert\text{-C}_4\text{H}_9$	47°/0.02 84°–86°/1 254°	1.240	1.5130 1.5051	14, 193
$(\text{C}_2\text{H}_5)_3\text{SnS-iso-C}_5\text{H}_{11}$	96°–97°/1 285 (dec)	1.188	1.5060	193
$(\text{C}_2\text{H}_5)_3\text{SnS-}n\text{-C}_7\text{H}_{15}$	134°–135°/1		1.5006	196
$(\text{C}_2\text{H}_5)_3\text{SnSCH}_2\text{C}_6\text{H}_5$	138°–140°/1 260°	1.304	1.5682 1.5675	193, 196
$(\text{C}_2\text{H}_5)_3\text{SnSCH}_2\text{CO}_2\text{H}$				P77
$(\text{C}_2\text{H}_5)_3\text{SnSCH}_2\text{CO}_2\text{C}_2\text{H}_5$				223
$(\text{C}_2\text{H}_5)_3\text{SnSCH}_2\text{CO}_2\text{-}n\text{-C}_{10}\text{H}_{21}$				P77
$(\text{C}_2\text{H}_5)_3\text{SnSCH=NC}_6\text{H}_5$	115°–116°/0.2		1.5910	160
$(\text{C}_2\text{H}_5)_3\text{SnSC}_6\text{H}_5$	150°/1.7 138°–140°/1	1.314 1.316	1.5794 1.5828	14, 196
$(\text{C}_2\text{H}_5)_3\text{SnSC}_6\text{H}_4\text{CH}_3\text{-}o$	132°–135°/1 292° (dec)	1.295	1.5740 1.5720	193, 196
$(\text{C}_2\text{H}_5)_3\text{SnSC}_6\text{H}_4\text{CH}_3\text{-}m$	132°–134°/1 288°	1.283	1.5705	193
$(\text{C}_2\text{H}_5)_3\text{SnSC}_6\text{H}_4\text{CH}_3\text{-}p$	125°–126°/1 129°–132°/1 300°	1.288	1.5712	193, 195, 196
$(\text{C}_2\text{H}_5)_3\text{SnSC}_{10}\text{H}_7\text{-}\beta$	189°–190°/1	1.3231	1.5308	196

TABLE 1—*Continued*

Compound	M.p. (°C)	B.p. (°C)/mm	d_D^{20}	n_D^{20}	References
<i>Tin</i> (continued)					
(C ₂ H ₅) ₃ SnSC ₂ N ₂ S ₂ H	47°–49°				P108
(C ₂ H ₅) ₂ (C ₂ H ₃)SnS- <i>n</i> -C ₁₂ H ₂₅			1.06	1.498 (21°)	P33
(<i>n</i> -C ₃ H ₇) ₃ SnS- <i>n</i> -C ₇ H ₁₅		158°–160°/1		1.4981	194
(<i>n</i> -C ₃ H ₇) ₃ SnS- <i>n</i> -C ₁₀ H ₂₁		180°–183°/1		1.4998	194
(<i>n</i> -C ₃ H ₇) ₃ SnSCH ₂ C ₆ H ₅		165°–167°/1		1.5558	194
(<i>n</i> -C ₃ H ₇) ₃ SnSC ₆ H ₅		157°–159°/1		1.5626	195
(<i>n</i> -C ₃ H ₇) ₃ SnSC ₆ H ₄ CH ₃ - <i>p</i>		157°–159°/1		1.5516	193–195
				1.5602	
(<i>iso</i> -C ₃ H ₇) ₃ SnS- <i>n</i> -C ₇ H ₁₅		155°–157°/1		1.5045	194
(<i>iso</i> -C ₃ H ₇) ₃ SnS- <i>n</i> -C ₁₀ H ₂₁		192°–195°/1		1.5010	194
(<i>iso</i> -C ₃ H ₇) ₃ SnSCH ₂ C ₆ H ₅		167°–170°/1		1.5497	194
(<i>iso</i> -C ₃ H ₇) ₃ SnSC ₆ H ₅		138°–139°/1		1.5676	194
(<i>iso</i> -C ₃ H ₇) ₃ SnSC ₆ H ₄ CH ₃ - <i>p</i>		157°–158°/1		1.5648	194
(<i>n</i> -C ₄ H ₉) ₂ Sn(Cl)S- <i>n</i> -C ₄ H ₉		96°–98°/1			213
(<i>n</i> -C ₄ H ₉) ₂ Sn(O- <i>n</i> -C ₄ H ₉)S- <i>n</i> -C ₈ H ₁₇					P18
(<i>n</i> -C ₄ H ₉) ₂ Sn(OCOCH=CHCO ₂ C ₁₈ H ₃₅)(SC ₁₂ H ₂₅)			1.038	1.4890	P90
(<i>n</i> -C ₄ H ₉) ₂ Sn(OCOC ₁₁ H ₂₃)(SC ₁₂ H ₂₅)			1.036	1.4834	P90
(<i>n</i> -C ₄ H ₉) ₃ SnSC(S)OCH ₃					50
(<i>n</i> -C ₄ H ₉) ₃ SnSC(S)O- <i>iso</i> -C ₃ H ₇					P92
(<i>n</i> -C ₄ H ₉) ₃ SnSC(S)OSn(<i>n</i> -C ₄ H ₉) ₃					50
(<i>n</i> -C ₄ H ₉) ₃ SnSC(S)N(C ₂ H ₅) ₂					P24
(<i>n</i> -C ₄ H ₉) ₃ SnSCH ₂ CO ₂ H					P77
(<i>n</i> -C ₄ H ₉) ₃ SnSCH ₂ CO ₂ - <i>n</i> -C ₁₀ H ₂₁					P3, P77
(<i>n</i> -C ₄ H ₉) ₃ SnS(CH ₂) ₂ CONH- <i>n</i> -C ₅ H ₁₁					P7, P41, P61
(<i>n</i> -C ₄ H ₉) ₃ SnS- <i>n</i> -C ₁₂ H ₂₅					P2, P76, P83

$(n\text{-C}_4\text{H}_9)_3\text{SnSSO}_2\text{CH}_3$		98°–100°/0.2		P100
$(n\text{-C}_4\text{H}_9)_3\text{SnSC}_2\text{N}_2\text{S}_2\text{H}$	52°–55°			P108
$(\text{C}_6\text{H}_5)_3\text{SnS-}n\text{-C}_{12}\text{H}_{25}$				P2, P76, P83
$(\text{C}_6\text{H}_5)_3\text{SnSCH}_2\text{CO}_2\text{-}n\text{-C}_{10}\text{H}_{21}$				P77
$(\text{C}_6\text{H}_5)_3\text{SnSCH}_2\text{C}_6\text{H}_5$	84°			69
$(\text{C}_6\text{H}_5)_3\text{SnSCOC}_6\text{H}_5$	108°–109°			69, 216
$(\text{C}_6\text{H}_5)_3\text{SnSC}_6\text{H}_5$	102°–103°			49, 69, 165, 203
$(\text{C}_6\text{H}_5)_3\text{SnSC}_6\text{H}_4\text{Cl-}p$	96°–97°			69
$(\text{C}_6\text{H}_5)_3\text{SnSC}_{10}\text{H}_7\text{-}\beta$				165
$(\text{C}_6\text{H}_5)_3\text{SnSC(S)NHC}_6\text{H}_5$				138
$(\text{C}_6\text{H}_5)_3\text{SnSSO}_2\text{CH}_3$	350°			P100
$(p\text{-iso-C}_3\text{H}_7\text{C}_6\text{H}_4\text{CH}_2)_3\text{SnS}_2\text{C}_7\text{H}_4\text{N}$	65°			68
<i>Lead</i>				
$(\text{CH}_3)_3\text{PbSCH}_3$		32°/0.01	1.6131	7, P97, P103
		43°/0.75	1.6116	
$(\text{CH}_3)_3\text{PbSC}_2\text{H}_5$		36°/0.05	1.5918	14
$(\text{CH}_3)_3\text{PbSCH}_2\text{CO}_2\text{CH}_3$				P98
$(\text{CH}_3)_2\text{Pb(C}_2\text{H}_5)_2\text{SCH}_2\text{CONH}_2$				P99
$(\text{CH}_3)_2\text{Pb}(n\text{-C}_7\text{H}_{15})\text{SCH}_2\text{CONH}_2$				P99
$(\text{C}_2\text{H}_5)_3\text{PbSC}_2\text{H}_5$		76°–78°/0.075		102, 150
$(\text{C}_2\text{H}_5)_3\text{PbSCOCH}_3$	45			103
$(\text{C}_2\text{H}_5)_3\text{PbS-}n\text{-C}_7\text{H}_{15}$				88
$(\text{C}_2\text{H}_5)_3\text{PbSCH}_2\text{CONH}_2$				P99
$(\text{C}_2\text{H}_5)_3\text{PbSC}_6\text{H}_5$				88, 102
$(\text{C}_2\text{H}_5)_2\text{Pb(iso-C}_3\text{H}_7)\text{SCH}_2\text{CONH}_2$				P99
$(n\text{-C}_4\text{H}_9)_3\text{PbSCH}_2\text{CONH}_2$				P99
$(\text{C}_6\text{H}_5)_3\text{PbSCH}_3$	108°–109°			106
$(\text{C}_6\text{H}_5)_3\text{PbSC}_2\text{H}_5$	67°–68°			106
$(\text{C}_6\text{H}_5)_3\text{PbSC}_3\text{H}_5$	45°			69
$(\text{C}_6\text{H}_5)_3\text{PbS-}n\text{-C}_3\text{H}_7$	57°–58°			106

TABLE 1—*Continued*

Compound	M.p.(°C)	B.p.(°C)/mm	d_D^{20}	n_D^{20}	References
<i>Lead (continued)</i>					
(C ₆ H ₅) ₃ PbS- <i>n</i> -C ₄ H ₉				1.6500	106
(C ₆ H ₅) ₃ PbSCOHCH ₃	92°–93°				106
(C ₆ H ₅) ₃ PbSCH ₂ CO ₂ CH ₃	87°–88°				69
(C ₆ H ₅) ₃ PbSCH ₂ CONH ₂	124°–125°				69
(C ₆ H ₅) ₃ PbS(CH ₂) ₂ OH	78°–79°				69
(C ₆ H ₅) ₃ PbS(CH ₂) ₂ NH ₂	40°				69
(C ₆ H ₅) ₃ PbSCH ₂ C ₆ H ₅	82°–83°				106
(C ₆ H ₅) ₃ PbSCOC ₆ H ₅	93°–94°				106
(C ₆ H ₅) ₃ PbSC ₆ H ₅	106°–107°				106
(C ₆ H ₅) ₃ PbSC ₆ H ₄ Cl- <i>p</i>	102°				69
(C ₆ H ₅) ₃ PbSC ₆ H ₄ NO ₂ - <i>p</i>	111°				69
(C ₆ H ₅) ₃ PbSC ₆ H ₄ NH ₂ - <i>p</i>	135°–136°				69
(C ₆ H ₅) ₃ PbSC ₆ F ₅	91°				69
(C ₆ H ₅) ₃ PbS-17- β -mercaptotestosterone	152°				69
	125°				

TABLE 2
COMPOUNDS OF GENERAL FORMULA $R_2M(SR')_2$

Compound	M.p. (°C)	B.p. (°C)/mm	d_4^{20}	n_D^{20}	References
<i>Silicon</i>					
$(CH_3)_2Si(SCH_3)_2$		52°–54°/7			107
$(CH_3)_2Si(S-n-C_{12}H_{25})_2$	29.5°–30°	210°/0.01			47
$(CH_3)_2Si(S-n-C_5H_{11})SC_6H_5$					P111
$(C_2H_5)_2Si(SC_2H_5)_2$		81°–82°/0.1			199
$(C_2H_5)_2Si(S-n-C_{10}H_{21})_2$					P59
<i>Germanium</i>					
$(C_6H_5)_2Ge(SCH_3)_2$		132°–135°/0.2			104, 107
$(C_6H_5)_2Ge(SC_3H_5)_2$				1.6229 (28.5°)	69
$(C_6H_5)_2Ge(S-n-C_{11}H_{23})_2$				1.5343 (28.5°)	69
$(C_6H_5)_2Ge(SCH_2CONH_2)_2$	140°				69
$(C_6H_5)_2Ge[S(CH_2)_2OH]_2$					69
$(C_6H_5)_2Ge(SCH_2C_6H_5)_2$	50°–51°				69
$(C_6H_5)_2Ge(SCOC_6H_5)_2$	150°–151°				69
$(C_6H_5)_2Ge(SC_6H_5)_2$				1.6776 (22°)	69
$(C_6H_5)_2Ge(SC_6H_4Cl-p)_2$				1.6751 (22°)	69
$(C_6H_5)_2Ge(SC_6H_4NH_2-p)_2$	115°				69
$(C_6H_5)_2Ge(SC_6H_4NO_2-p)_2$	114°–115°				69
$(C_6H_5)_2Ge(SC_{10}H_7-\beta)_2$	90°–91°				69
<i>Tin</i>					
$(CH_3)_2Sn(SCH_3)_2$		44°/0.05	1.547	1.6003	14
$(CH_3)_2Sn(SC_2H_5)_2$		58°/0.07	1.440	1.5713	14
$(CH_3)_2Sn(S-n-C_3H_7)_2$		74°/0.1	1.323	1.5498	14

TABLE 2—Continued

Compound	M.p. (°C)	B.p. (°C)/mm	d_4^{20}	n_D^{20}	References
<i>Tin</i> (continued)					
(CH ₃) ₂ Sn(S- <i>n</i> -C ₄ H ₉) ₂		81°/0.1	1.280	1.5400	14
(CH ₃) ₂ Sn(S- <i>n</i> -C ₈ H ₁₇) ₂		166°/0.2	1.092	1.5129	14
(CH ₃) ₂ Sn(S- <i>n</i> -C ₁₂ H ₂₅) ₂					P2, P76, P83
(CH ₃) ₂ Sn[S(CH ₂) ₂ CO ₂ - <i>n</i> -C ₁₈ H ₃₇] ₂					P13
(CH ₃) ₂ Sn(SCOCH ₃) ₂					P101
(CH ₃) ₂ Sn(SC ₆ H ₅) ₂	38°–39°	130°–135°/0.001			6
(C ₂ H ₅) ₂ Sn(SCH ₃) ₂		61°/0.1	1.440	1.5793	14
(C ₂ H ₅) ₂ Sn(SC ₂ H ₅) ₂		94°/0.05	1.319	1.5572	14
(C ₂ H ₅) ₂ Sn(SC ₆ H ₄ - <i>tert</i> -C ₄ H ₉ - <i>p</i>) ₂					P36
(<i>n</i> -C ₈ H ₁₇) ₂ Sn[S(CH ₂) ₂ OCO- <i>n</i> -C ₈ H ₁₇] ₂					P81
(<i>n</i> -C ₈ H ₁₇) ₂ Sn(SC ₆ H ₅) ₂		226°–230°/1		1.6298	195
(<i>n</i> -C ₄ H ₉) ₂ Sn(SC ₂ H ₅) ₂					P76
(<i>n</i> -C ₄ H ₉) ₂ Sn(S- <i>n</i> -C ₄ H ₉) ₂					P2, P76, P83
(<i>n</i> -C ₄ H ₉) ₂ Sn(S- <i>sec</i> -C ₄ H ₉) ₂					P2, P76, P83
(<i>n</i> -C ₄ H ₉) ₂ Sn(S- <i>iso</i> -C ₄ H ₉) ₂					P2, P76, P83
(<i>n</i> -C ₄ H ₉) ₂ Sn(S- <i>n</i> -C ₅ H ₁₁) ₂					P2, P76, P83
(<i>n</i> -C ₄ H ₉) ₂ Sn(S- <i>n</i> -C ₆ H ₁₃) ₂					P2, P76, P83
(<i>n</i> -C ₄ H ₉) ₂ Sn(S- <i>tert</i> -C ₆ H ₁₃) ₂					P2, P76, P83
(<i>n</i> -C ₄ H ₉) ₂ Sn(S- <i>n</i> -C ₇ H ₁₅) ₂					P2, P76, P83
(<i>n</i> -C ₄ H ₉) ₂ Sn(S- <i>n</i> -C ₈ H ₁₇) ₂					54, 191, P2, P76, P83
(<i>n</i> -C ₄ H ₉) ₂ Sn(S- <i>n</i> -C ₉ H ₁₉) ₂					P2, P76, P83
(<i>n</i> -C ₄ H ₉) ₂ Sn(S- <i>n</i> -C ₁₀ H ₂₁) ₂					P2, P76, P83

$(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{S-}n\text{-C}_{12}\text{H}_{25})_2$	160°/0.0001	1.4992 1.5011	156, 183 P2, P4, P23, P30, P35, P39, P46, P63, P64, P65, P75, P76, P83
$(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{S-}n\text{-C}_{14}\text{H}_{29})_2$			P2, P76, P83
$(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{S-}n\text{-C}_{16}\text{H}_{33})_2$			P2, P76, P83
$(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{S-}n\text{-C}_{18}\text{H}_{37})_2$			P88
$(n\text{-C}_4\text{H}_9)_2\text{Sn}[\text{S}(\text{CH}_2)_2\text{OH}]_2$			P12, P82
$(n\text{-C}_4\text{H}_9)_2\text{Sn}[\text{S}(\text{CH}_2)_2\text{OCO-}n\text{-C}_{11}\text{H}_{23}]_2$			P17
$(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{SCH}_2\text{CONH-}n\text{-C}_5\text{H}_{11})_2$			P7, P41, P61
$(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{SCH}_2\text{CO}_2\text{-}n\text{-C}_9\text{H}_{19})_2$			P3, P58
$(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{SCH}_2\text{CONH-}n\text{-C}_8\text{H}_{17})_2$			P7, P61
$(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{SC}_6\text{H}_5)_2$			P2, P43, P76, P83
$(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{SC}_6\text{H}_4\text{CH}_3\text{-}p)_2$			P2, P76, P83
$(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{SC}_6\text{H}_4\text{-}n\text{-C}_9\text{H}_{19}\text{-}p)_2$			P36
$(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{SC}_6\text{H}_4\text{NH}_2\text{-}o)_2$			P2, P76, P83
$(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{SC}_6\text{H}_4\text{-}tert\text{-C}_4\text{H}_9\text{-}p)_2$			P36
$(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{SC}_7\text{H}_4\text{NS})_2$			P2, P67, P76, P83
$(n\text{-C}_4\text{H}_9)_2\text{Sn}[\text{SCH}_2\text{CON}(\text{CH}_2)_2\text{OCH}_2\text{CH}_2]_2$			P7, P41, P61
$(n\text{-C}_4\text{H}_9)_2\text{Sn}[\text{SCH}(n\text{-C}_4\text{H}_9)\text{CO}_2\text{-}n\text{-C}_4\text{H}_9]_2$			P77
$(n\text{-C}_4\text{H}_9)_2\text{Sn}[\text{S}(\text{CH}_2)_7\text{CO}_2\text{-}n\text{-C}_4\text{H}_9]_2$			P77
$(n\text{-C}_4\text{H}_9)_2\text{Sn}[\text{SCH}(n\text{-C}_5\text{H}_{11})\text{CO}_2\text{-}n\text{-C}_4\text{H}_9]_2$			P77
$(n\text{-C}_4\text{H}_9)_2\text{Sn}[\text{SCH}(n\text{-C}_{10}\text{H}_{21})\text{CO}_2\text{-}n\text{-C}_4\text{H}_9]_2$			P77
$(n\text{-C}_4\text{H}_9)_2\text{Sn}[\text{S}(\text{CH}_2)_{11}\text{CO}_2\text{-}n\text{-C}_4\text{H}_9]_2$			P77
$(n\text{-C}_4\text{H}_9)_2\text{Sn}[\text{SCH}(n\text{-C}_{14}\text{H}_{29})\text{CO}_2\text{-}n\text{-C}_4\text{H}_9]_2$			P77
$(n\text{-C}_4\text{H}_9)_2\text{Sn}[\text{SCH}(n\text{-C}_7\text{H}_{15})\text{CO}_2\text{-}n\text{-C}_4\text{H}_9]_2$			P77
$(n\text{-C}_4\text{H}_9)_2\text{Sn}[\text{SCH}(n\text{-C}_{16}\text{H}_{33})\text{CO}_2\text{-}n\text{-C}_4\text{H}_9]_2$			P77
$(n\text{-C}_4\text{H}_9)_2\text{Sn}[\text{S}(\text{CH}_2)_2\text{CO}_2\text{CH}_2\text{CH}(n\text{-C}_4\text{H}_9)\text{-}n\text{-C}_6\text{H}_{13}]_2$			P77
$(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{SCH}_2\text{CO}_2\text{C}_6\text{H}_{11})_2$			P77
$(n\text{-C}_4\text{H}_9)_2\text{Sn}[\text{SCH}_2\text{CO}_2(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{CO}_2\text{-}n\text{-C}_{11}\text{H}_{23}]_2$			P77
$(n\text{-C}_4\text{H}_9)_2\text{Sn}[\text{SCH}_2\text{CO}_2\text{CH}_2\text{C}_{16}\text{H}_{23}\text{CH}(\text{CH}_3)_2]_2$			P77

TABLE 2—Continued

Compound	M.p. (°C)	B.p. (°C)/mm	d_4^{20}	n_D^{20}	References
<i>Tin</i> (continued)					
(<i>n</i> -C ₄ H ₉) ₂ Sn[SCH ₂ CO ₂ CH ₂ OCO(CH ₂) ₇ CH=CHCH ₂ CH(OH)- <i>n</i> -C ₆ H ₁₃] ₂					P77
(<i>n</i> -C ₄ H ₉) ₂ Sn[SC(C ₂ H ₅)(<i>n</i> -C ₄ H ₉)CO ₂ C ₂ H ₅] ₂					P77
(<i>n</i> -C ₄ H ₉) ₂ Sn[SC(C ₆ H ₅) ₂ CO ₂ C ₂ H ₅] ₂					P77
(<i>n</i> -C ₄ H ₉) ₂ Sn[S(CH ₂) ₁₁ CO ₂ C ₂ H ₅] ₂					P75
(<i>n</i> -C ₄ H ₉) ₂ Sn[S(CH ₂) ₂ CO ₂ - <i>n</i> -C ₈ H ₁₇] ₂					P40, P57
(<i>n</i> -C ₄ H ₉) ₂ Sn(SCH ₂ CO ₂ - <i>iso</i> -C ₈ H ₁₇) ₂					P75
(<i>n</i> -C ₄ H ₉) ₂ Sn(SCH ₂ CO ₂ - <i>n</i> -C ₉ H ₁₉) ₂					P25
(<i>n</i> -C ₄ H ₉) ₂ Sn[S(CH ₂) ₄ OCO- <i>n</i> -C ₈ H ₁₇] ₂					P81
(<i>n</i> -C ₄ H ₉) ₂ Sn[S(CH ₂) ₄ OCO- <i>iso</i> -C ₈ H ₁₇] ₂					P81
(<i>n</i> -C ₄ H ₉) ₂ Sn[S(CH ₂) ₂ OCOC ₁₇ H ₃₅ CH(CH ₃) ₂] ₂					P81
(<i>n</i> -C ₄ H ₉) ₂ Sn[S(CH ₂) ₂ OCO- <i>n</i> -C ₁₉ H ₃₉] ₂					P81
(<i>n</i> -C ₄ H ₉) ₂ Sn[<u>SCHOCO(CH₂)₄CO₂CH₂]</u> ₂					P81
(<i>n</i> -C ₄ H ₉) ₂ Sn[SCH ₂ CO ₂ CH ₂ CH(C ₂ H ₅)- <i>n</i> -C ₄ H ₉] ₂				1.5075	P35
(<i>n</i> -C ₄ H ₉) ₂ Sn[S(CH ₂) ₂ CO ₂ CH ₂ CH(C ₂ H ₅)- <i>n</i> -C ₄ H ₉] ₂				1.5046	P35
(<i>n</i> -C ₄ H ₉) ₂ Sn[S(CH ₂) ₂ OCO- <i>n</i> -C ₁₁ H ₂₃] ₂					P81
(<i>n</i> -C ₄ H ₉) ₂ Sn[S(CH ₂) ₂ OCO- <i>n</i> -C ₈ H ₁₇] ₂					P81
(<i>n</i> -C ₄ H ₉) ₂ Sn[S(CH ₂) ₂ CO ₂ - <i>iso</i> -C ₈ H ₁₇] ₂					P81
(<i>n</i> -C ₄ H ₉) ₂ Sn[SCH ₂ CO ₂ (CH ₂) ₂ C ₆ H ₅] ₂					P77
(<i>n</i> -C ₄ H ₉) ₂ Sn[SCH(CO ₂ H)CH ₂ CO ₂ H] ₂					P77
(<i>n</i> -C ₄ H ₉) ₂ Sn[SCH ₂ CO ₂ (CH ₂) ₂ CH(CH ₃)CH ₂ - <i>tert</i> -C ₄ H ₉] ₂					P77
(<i>n</i> -C ₄ H ₉) ₂ Sn[SCH(C ₂ H ₅)CO ₂ CH ₂ CH ₂ CH(CH ₃)CH ₂ - <i>tert</i> -C ₄ H ₉] ₂					P77
(<i>n</i> -C ₄ H ₉) ₂ Sn[SCH(<i>n</i> -C ₄ H ₉)CO ₂ (CH ₂) ₂ CH(CH ₃)CH ₂ - <i>tert</i> -C ₄ H ₉] ₂					P77

$(n\text{-C}_4\text{H}_9)_2\text{Sn}[\text{S}(\text{CH}_2)_5\text{CO}_2(\text{CH}_2)_2\text{CH}(\text{CH}_3)\text{CH}_2\text{-tert-C}_4\text{H}_9]_2$		<i>P77</i>
$(n\text{-C}_4\text{H}_9)_2\text{Sn}[\text{SC}(\text{C}_2\text{H}_5)_2\text{CO}_2(\text{CH}_2)_2\text{CH}(\text{CH}_3)\text{CH}_2\text{-tert-C}_4\text{H}_9]_2$		<i>P77</i>
$(n\text{-C}_4\text{H}_9)_2\text{Sn}[\text{SCH}(\text{CH}_3)\text{CO}_2(\text{CH}_2)_2\text{CH}(\text{CH}_3)\text{CH}_2\text{-tert-C}_4\text{H}_9]_2$		<i>P77</i>
$(n\text{-C}_4\text{H}_9)_2\text{Sn}[\text{S}(\text{CH}_2)_2\text{CO}_2(\text{CH}_2)_2\text{CH}(\text{CH}_3)\text{CH}_2\text{-tert-C}_4\text{H}_9]_2$		<i>P77</i>
$(n\text{-C}_4\text{H}_9)_2\text{Sn}[\text{SCH}(n\text{-C}_3\text{H}_7)\text{CO}_2(\text{CH}_2)_2\text{CH}(\text{CH}_3)\text{CH}_2\text{-tert-C}_4\text{H}_9]_2$		<i>P77</i>
$(n\text{-C}_4\text{H}_9)_2\text{Sn}[\text{S}(\text{CH}_2)_4\text{CO}_2(\text{CH}_2)\text{CH}(\text{CH}_3)\text{CH}_2\text{-tert-C}_4\text{H}_9]_2$		<i>P77</i>
$(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{SCH}_2\text{CO}_2\text{-}n\text{-C}_{12}\text{H}_{25})_2$		<i>P77</i>
$(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{SCOCH}_3)_2$		<i>P43</i>
$(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{SSO}_2\text{CH}_3)_2$	106°	<i>P100</i>
$(n\text{-C}_4\text{H}_9)_2\text{Sn}[\text{SCO}(\text{CH}_2)_n\text{CH}_3]_2$ ($n = 0\text{--}10$)		<i>P94</i>
$(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{SCOR})_2$ ($\text{R} = \text{C}_6\text{H}_5, \text{C}_6\text{H}_5\text{CH}_2, \text{CH}_3\text{C}_6\text{H}_4$)		<i>P94</i>
$(\text{iso-C}_4\text{H}_9)_2\text{Sn}[\text{SCH}_2\text{CO}_2\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{-}n\text{-C}_4\text{H}_9]_2$	1.5033	<i>P35</i>
$(n\text{-C}_5\text{H}_{11})_2\text{Sn}(\text{S-}n\text{-C}_{12}\text{H}_{25})_2$		<i>P76, P83</i>
$(n\text{-C}_6\text{H}_{13})_2\text{Sn}(\text{SCSNH}_2)_2$		<i>P24</i>
$(n\text{-C}_8\text{H}_{17})_2\text{Sn}(\text{S-}n\text{-C}_{12}\text{H}_{25})_2$		<i>P50, P88</i>
$(n\text{-C}_8\text{H}_{17})_2\text{Sn}(\text{SCH}_2\text{C}_6\text{H}_5)_2$		<i>P22</i>
$(n\text{-C}_8\text{H}_{17})_2\text{Sn}[\text{SCH}_2\text{CO}_2\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{-}n\text{-C}_4\text{H}_9]_2$	1.4992	<i>P35</i>
$(n\text{-C}_8\text{H}_{17})_2\text{Sn}(\text{SCH}_2\text{CO}_2\text{-}n\text{-C}_{18}\text{H}_{37})_2$	1.4992	<i>P35</i>
$(n\text{-C}_8\text{H}_{17})_2\text{Sn}(\text{SCH}_2\text{CO}_2\text{-}n\text{-C}_4\text{H}_9)_2$	1.5070	<i>P35</i>
$(n\text{-C}_8\text{H}_{17})_2\text{Sn}\{\text{SCH}[\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{-}n\text{-C}_4\text{H}_9]\text{CO}_2\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{-}n\text{-C}_4\text{H}_9\}_2$	1.4892	<i>P35</i>
$(n\text{-C}_8\text{H}_{17})_2\text{Sn}(\text{SC}_6\text{H}_5)_2$	1.5688	<i>P35</i>
$(n\text{-C}_{12}\text{H}_{25})_2\text{Sn}(\text{S-}n\text{-C}_5\text{H}_{11})_2$		<i>P2, P76, P83</i>
$(n\text{-C}_{12}\text{H}_{25})_2\text{Sn}(\text{SCH}_2\text{C}_6\text{H}_5)_2$	1.5496	<i>P2, P35, P76, P83</i>
$(n\text{-C}_{12}\text{H}_{25})_2\text{Sn}(\text{S-}n\text{-C}_{12}\text{H}_{25})_2$		<i>P2, P76, P83</i>
$(n\text{-C}_{12}\text{H}_{25})_2\text{Sn}(\text{SCH}_2\text{CO}_2\text{-}n\text{-C}_4\text{H}_9)_2$		<i>P77</i>
$(n\text{-C}_{12}\text{H}_{25})_2\text{Sn}[\text{S}(\text{CH}_2)_3\text{CO}_2\text{-}n\text{-C}_4\text{H}_9]_2$		<i>P40, P57</i>
$(n\text{-C}_{12}\text{H}_{25})_2\text{Sn}(\text{SC}_6\text{H}_4\text{-tert-C}_4\text{H}_9\text{-}p)_2$		<i>P36</i>

TABLE 2—continued

Compound	M.p. (°C)	B.p. (°C)/mm	d_4^{20}	n_D^{20}	References
<i>Tin</i> (continued)					
(C ₆ H ₅) ₂ Sn(S- <i>n</i> -C ₁₂ H ₂₅) ₂					P2, P39, P63, P76, P83
(C ₆ H ₅) ₂ Sn(SCH ₂ C ₆ H ₅) ₂					135, P2, P76, P83
(C ₆ H ₅) ₂ Sn(SC ₆ H ₅) ₂	65				36, 69, 203
(C ₆ H ₅) ₂ Sn(SCOC ₆ H ₅) ₂					217
(C ₆ H ₅) ₂ Sn(SC ₆ H ₄ - <i>tert</i> -C ₄ H ₉ - <i>p</i>) ₂					P36
(C ₆ H ₅ CH ₂) ₂ Sn(SC ₆ H ₄ - <i>tert</i> -C ₄ H ₉ - <i>p</i>) ₂					P36
(<i>p</i> -iso-C ₃ H ₇ C ₆ H ₄ CH ₂) ₂ Sn(SC ₇ H ₄ NS) ₂	93°–95°				68
<i>Lead</i>					
(C ₂ H ₅) ₂ Pb(SCOCH ₃) ₂	85°				103
(C ₆ H ₅) ₂ Pb(SC ₆ H ₅) ₂	75°				69
(C ₆ H ₅) ₂ Pb(SC ₆ H ₄ Cl- <i>p</i>) ₂	71°–72°				69
(C ₆ H ₅) ₂ Pb(SC ₇ H ₄ NS) ₂	148°–150°				69

TABLE 3
COMPOUNDS OF GENERAL FORMULA RM(SR)₃

Compound	M.p. (°C)	B.p. (°C)/mm	d_4^{20}	n_D^{20}	References
<i>Silicon</i>					
CH ₃ Si(SCH ₃) ₃		45°/0.2			107
CH ₃ Si(S- <i>n</i> -C ₁₂ H ₂₅) ₃	33°–34°	220°–240°/0.0001			47, 48
C ₂ H ₅ Si(SC ₂ H ₅) ₃		115°/0.1			199
<i>n</i> -C ₁₂ H ₂₅ Si(SC ₂ H ₅) ₃		188°/2.5		1.5133	47, 48
<i>n</i> -C ₁₂ H ₂₅ Si(S- <i>n</i> -C ₁₂ H ₂₅) ₃	12°–14°	130°–140°/0.001		1.4825	47, 48
C ₆ H ₅ CH ₂ Si(S- <i>n</i> -C ₈ H ₁₇) ₃					P59
α-SH ₃ C ₄ Si(S- <i>n</i> -C ₁₀ H ₂₁) ₃					P59

<i>Germanium</i>				
$C_6H_5Ge(SCH_3)_3$	110°/0.2			107
<i>Tin</i>				
$CH_3Sn(SCH_3)_3$	75°/0.01	1.630	1.6352 (22°)	6
$CH_3Sn(SC_2H_5)_3$	90°/0.05	1.469	1.5972	14
$CH_3Sn(S-n-C_3H_7)_3$	95°/0.001	1.337	1.5684	14
$CH_3Sn(S-n-C_4H_9)_3$			1.5541	P69
$CH_3Sn(S-sec-C_5H_{11})_3$			1.5452	P69
$CH_3Sn(S-n-C_{12}H_{25})_3$				P2, P76, P83
$CH_3Sn(S-tert-C_{12}H_{25})_3$				P69
$CH_3Sn(S-n-C_{18}H_{37})_3$	50°–60°			P69
$CH_3Sn(SCH_2CH_2OH)_3$				P69
$CH_3Sn(SCH_2C_6H_4Cl-p)_3$				P69
$CH_3Sn(SCH_2C_6H_4OH)_3$	143°–145°			P69
$CH_3Sn(SC_6H_4.O.C_6H_4SH-p)_3$				P69
$CH_3Sn(SC_6H_4COOCH_3)_3$			1.6579	P69
$CH_3Sn(SC_{10}H_7-\alpha)_3$			1.71	P69
$C_2H_5Sn(SCH_3)_3$	66°/0.001	1.548	1.6232	14
$C_2H_5Sn(S-n-C_{12}H_{25})_3$				P2, P76, P83
$iso-C_3H_7Sn[S(CH_2)_2OCOC_6H_4COOH]_3$	140°			P11, P42
$iso-C_3H_7Sn(SCH_2CH_2CH_2CONH-n-C_4H_9)_3$	130°			P7, P41, P61
$iso-C_3H_7Sn(SCH_2CH_2OCO-n-C_8H_{17})_3$	100°			P81
$n-C_4H_9Sn(S-n-C_4H_9)_3$			1.542	P69
$n-C_4H_9Sn(S-n-C_{12}H_{25})_3$				P2
$n-C_4H_9Sn(S-tert-C_{12}H_{25})_3$				P69
$n-C_4H_9Sn(SCH_2COOH)_3$				P77
$n-C_4H_9Sn(SCH_2COO-n-C_{10}H_{21})_3$				P78
$n-C_4H_9Sn(SC_6H_4COOCH_3-p)_3$				P69
$n-C_4H_9Sn(SCH_2C_6H_4OH-p)_3$			1.6540	P69
$tert-C_4H_9Sn(SCH_2CH_2OH)_3$				P81
$C_6H_5Sn(S-n-C_4H_9)_3$			1.5710	P69
$C_6H_5Sn(SCH_2C_6H_4OH-p)_3$			1.6890	P69

TABLE 4
COMPOUNDS OF GENERAL FORMULA $M(SR)_4$

Compound	M.p. (°C)	B.p. (°C)/mm	d_4^{25}	n_D^{25}	References
<i>Silicon</i>					
$Si(SCH_3)_4$	31°	144°–146°/12 66°/0.3	1.1888 (35°)	1.5989 (35°)	32, 37, 107, 199
$Si(SC_2H_5)_4$	–5.8°	169°–171°/12	1.0860	1.5638	37, 199
$Si(S-n-C_3H_7)_4$		204°–206°/17	1.0328	1.5431	37
$Si(S-iso-C_3H_7)_4$	33.5°	176°–178°/13	1.0099 (35°)	1.5350 (35°)	37, 41
$Si(S-n-C_4H_9)_4$		210°/4	0.9958	1.5292	38
$Si(S-iso-C_4H_9)_4$		183°/4	0.9886	1.5255	38
$Si(S-sec-C_4H_9)_4$		182°/4	1.0022	1.5354	38
$Si(S-tert-C_4H_9)_4$	160°–161°				34, 40
$Si(S-n-C_5H_{11})_4$		230°–232°/3–4	0.9739	1.5212	41
$Si(S-n-C_{12}H_{25})_4$	43°–44°				47, 48
$Si(S-n-C_{16}H_{33})_4$	50°–51°				41
$Si(SC_6H_{11})_4$	101.5°–102.5°				41
$Si(SC_6H_5)_4$	115°				38, 41, 199
$Si(SC_6H_4CH_3-p)_4$	129°				38, 41
$Si(SC_6H_4-tert-C_4H_9-p)_4$	185°–186°				38, 41
$(tert-C_4H_9S)_3SiSCH_3$	43°–44°	159°–160°/4			40
$(tert-C_4H_9S)_3SiSC_2H_5$	26°–27°	189°–191°/12			40
$(tert-C_4H_9S)_3SiS-n-C_3H_7$	62.5°				34
$(tert-C_4H_9S)_3SiS-iso-C_3H_7$	105°	161°–163°/3–4			40
$(tert-C_4H_9S)_3SiS-n-C_4H_9$		153°/1			34
$(tert-C_4H_9S)_3SiS-iso-C_4H_9$	77.5°	146°–148°/1			34
$(tert-C_4H_9S)_3SiS-sec-C_4H_9$	79°–80°	145°–147°/1			34
$(tert-C_4H_9S)_3SiSC_5H_{11}$	27°–29°	170°/2			34

$(tert\text{-C}_4\text{H}_9\text{S})_3\text{SiS-}tert\text{-C}_5\text{H}_{11}$	111.5°–114°				34
$(tert\text{-C}_4\text{H}_9\text{S})_3\text{SiSC}_5\text{H}_9$	105°				34
$(tert\text{-C}_4\text{H}_9\text{S})_3\text{SiSC}_6\text{H}_{11}$	65°				34
$(tert\text{-C}_4\text{H}_9\text{S})_2\text{Si(S-iso-C}_3\text{H}_7)_2$	62.5°	147°–148°/2			34
$tert\text{-C}_4\text{H}_9\text{SSi(S-iso-C}_3\text{H}_7)_3$	23.5°	160°–162°/3			34
<i>Germanium</i>					
$\text{Ge}(\text{SCH}_3)_4$	–3°	85°/0.4 140°/4	1.4364	1.6379	32, 39, 107
$\text{Ge}(\text{SC}_2\text{H}_5)_4$		151°/1 165°/5	1.2574	1.5886	1, 39
$\text{Ge}(\text{S-}n\text{-C}_3\text{H}_7)_4$		192°/5	1.1662	1.5612	39
$\text{Ge}(\text{S-iso-C}_3\text{H}_7)_4$	15°	162°–164°/4	1.1478	1.5535	39
$\text{Ge}(\text{S-}n\text{-C}_4\text{H}_9)_4$		198°/0.5 223°/5	1.1072	1.5439	1, 39
$\text{Ge}(\text{S-iso-C}_4\text{H}_9)_4$		200°/5	1.0984	1.5381	39
$\text{Ge}(\text{S-}sec\text{-C}_4\text{H}_9)_4$		201°/5	1.1119	1.5497	39
$\text{Ge}(\text{S-}tert\text{-C}_4\text{H}_9)_4$	172°–173°	170°/4 (sublimes)			39
$\text{Ge}(\text{S-}n\text{-C}_5\text{H}_{11})_4$		240°/3	1.0697	1.5336	41
$\text{Ge}(\text{S-}n\text{-C}_{16}\text{H}_{33})_4$	50°–51°				41
$\text{Ge}(\text{S-}n\text{-C}_6\text{H}_{11})_4$	84° (tetragonal) 88° (monoclinic)				41
$\text{Ge}(\text{SC}_6\text{H}_5)_4$	104°				39, 41, 166
$\text{Ge}(\text{SC}_6\text{H}_4\text{CH}_3\text{-}p)_4$	110°–111°				39, 41
$\text{Ge}(\text{SC}_6\text{H}_4\text{Br-}p)_4$	196.5°				39
$\text{Ge}(\text{SC}_6\text{H}_4\text{-}tert\text{-C}_4\text{H}_9\text{-}p)_4$	156°				41
<i>Tin</i>					
$\text{Sn}(\text{SCH}_3)_4$	31°	81°/0.001			32, 35
$\text{Sn}(\text{SC}_2\text{H}_5)_4$		200° 105°/0.001		1.6188 (20°)	35, 120

TABLE 4—Continued

68

E. W. ABEL and D. A. ARMITAGE

Compound	M.p. (°C)	B.p. (°C)/mm	d_4^{25}	n_D^{25}	References
<i>Tin</i> (continued)					
Sn(SC ₃ H ₅) ₄					36
Sn(S- <i>n</i> -C ₃ H ₇) ₄		123°/0.001		1.5851 (20°)	35
Sn(S-iso-C ₃ H ₇) ₄		92°/0.001		1.5789 (20°)	35
Sn[SCH ₂ C(CH ₂)CH ₃] ₄					36
Sn(S- <i>n</i> -C ₄ H ₉) ₄		136°/0.001		1.5539 (20°)	35
Sn(S-iso-C ₄ H ₉) ₄		126°/0.0005		1.5599 (20°)	35
Sn(S- <i>sec</i> -C ₄ H ₉) ₄		111°/0.001		1.5668 (20°)	35
Sn(S- <i>tert</i> -C ₄ H ₉) ₄	188°				35
Sn(S- <i>n</i> -C ₅ H ₁₁) ₄		162°/0.004		1.5475 (20°)	36
Sn(S- <i>tert</i> -C ₅ H ₁₁) ₄	44°				35
Sn(SC ₆ H ₁₁) ₄	54°				36
Sn(SC ₆ H ₁₃) ₄		200° (dec)			36
Sn(S- <i>n</i> -C ₁₂ H ₂₅) ₄	35.5°				36
Sn(S- <i>n</i> -C ₁₆ H ₃₃) ₄	53.5°				36
Sn(SCH ₂ C ₆ H ₅) ₄					36
Sn(SC ₆ H ₅) ₄	67°				36
Sn[SC ₆ H ₄ N(CH ₃) ₂ - <i>p</i>] ₄	159°				258
Sn[SC ₆ H ₄ NH ₂ - <i>p</i>] ₄	166°				258
Sn(SC ₆ H ₄ CH ₃ - <i>p</i>) ₄	100°				36
Sn(SC ₆ H ₄ Cl- <i>p</i>) ₄	189°				36
Sn(SC ₆ H ₄ Br- <i>p</i>) ₄	217°				36
Sn(SC ₆ H ₄ - <i>tert</i> -C ₄ H ₉ - <i>p</i>) ₄	106°				36

NOTE: Table 5 appears on page 71.

TABLE 6
COMPOUNDS OF GENERAL FORMULAS $(R_3M)_2S$ AND $R_3MSM'R_3$

Compound	M.p. (°C)	B.p. (°C)/mm	d_4^{20}	n_D^{20}	References
<i>Silicon</i>					
$(CH_3SiH_2)_2S$	$-120^\circ \pm 0.5^\circ$	$105^\circ \pm 0.5^\circ$ (estimated) 0°/9	0.885		78, 79
$[(CH_3)_2SiH]_2S$	$-146^\circ \pm 0.1^\circ$	$145^\circ \pm 1^\circ$ (estimated) 0°/9			80
$[(CH_3)_3Si]_2S$		163°	0.851	1.4572	3, 63, 71, 72
$[(CH_3)_3SiCH_2Si(CH_3)_2]_2S$	-98°	$117^\circ-118^\circ/3.5$	0.8774	1.4777	158, 234
$[(C_2H_5)_3SiCH_2Si(C_2H_5)_2]_2S$	-85°	$202^\circ-204^\circ/3$	0.9108	1.4980	158, 234
$[(C_2H_5)_3Si]_2S$		$128^\circ/7$ 279°		1.492 (12°)	63, 71, 72, 141, P111
$[(n-C_3H_7)_3Si]_2S$		$168^\circ/7$			141, P111
$[(n-C_4H_9)_3Si]_2S$		$160^\circ-163^\circ/1$			210
$[(C_6H_5)_3Si]_2S$	142°				46
<i>Germanium</i>					
$[(CH_3)_3Ge]_2S$	-22°	40°/1 68°/12	1.278	1.4980 (22°)	7, 189
$[(C_2H_5)_3Ge]_2S$		$148^\circ-150^\circ/12$			59
$[(C_6H_5CH_2)_3Ge]_2S$	124°				59, 188
$[(C_6H_5)_3Ge]_2S$	138°				59, 104, 105, 219
$[(p-CH_3C_6H_4)_3Ge]_2S$	$156^\circ-157^\circ$				59
$[(C_6H_5C_6H_4)_3Ge]_2S$	238°				59

TABLE 6—*continued*

Compound	M.p. (°C)	B.p. (°C)/mm	d_4^{25}	n_D^{25}	References
<i>Tin</i>					
$[(CH_3)_3Sn]_2S$		235° 118°/18			101, 126, 132
$[(C_2H_5)_3Sn]_2S$		187°–188°/20 133°–137°/1	1.429	1.5468	24, 101, 132, 136, 137, 149, 195
$[(n-C_3H_7)_3Sn]_2S$		254°/16			101
$[(n-C_4H_9)_2SnCl]_2S$		110°–115°/1			213
$[(n-C_4H_9)_3Sn]_2S$		208°/1		1.518 (21°)	67, 70, 132, P21, P48
$[(C_6H_5CH_2)_3Sn]_2S$					P48
$[(C_6H_5)_3Sn]_2S$	141.5°–143°				138, 146, 161, 162, 165, 180, 216, 226, P27, P48
$[(p-C_2H_5OCOC_6H_4)_3Sn]_2S$	132°–133°				157
$[(p-is-C_3H_7C_6H_4CH_2)_3Sn]_2S$	65°				68
<i>Lead</i>					
$[(CH_3)_3Pb]_2S$					7, P96
$[(C_2H_5)_3Pb]_2S$			2.05	1.6249	62, 108, 121
$[(C_6H_5)_3Pb]_2S$	139°–140°				97, 127, 220
<i>Mixed</i>					
$(CH_3)_3SiSGe(CH_3)_3$	–27°	63°/10			189
$(CH_3)_3GeSSn(CH_3)_3$	–8°	89°–90°/12 51°–52°/1			189
$(C_6H_5)_3GeSSn(C_6H_5)_3$	136°				215, 216, 219
$(C_6H_5)_3GeSPb(C_6H_5)_3$	128°–129°				219
$(C_6H_5)_3SnSPb(C_6H_5)_3$	92°				215, 216, 220

TABLE 5
COMPOUNDS OF GENERAL FORMULA R_3MSH

Compound	M.p. (°C)	B.p. (°C)/mm	d_4^{20}	n_D^{20}	References
<i>Silicon</i>					
$(CH_3)_2Si(NHCH_3)SH$					P111
$(CH_3)_3SiSH$		77°–78°			3, 63, 141
$(CH_3)_3SiCH_2Si(CH_3)_2SH$		56°–60°/14	0.8632	1.4604	158, 234
$(C_2H_5)_3SiSH$		160°–167°			141, P111
$(C_2H_5)_3SiCH_2Si(C_2H_5)_2SH$		113°–114°/3.5	0.8989	1.4852	158, 234
$(n-C_3H_7)_3SiSH$		83°–84°/7			141
$(C_6H_5)_3SiSH$	103°	152°–158°/0.6			46, 61, 83
<i>Germanium</i>					
$(C_6H_5)_3GeSH$	110°–114°				104

TABLE 7
MISCELLANEOUS COMPOUNDS WITH M—S BONDS IN NONCYCLIC SYSTEMS

Compound	M.p. (°C)	References
<i>Silicon</i>		
$[(CH_3)_3Si]_2S_{2-9}$		198, P47
$[(C_2H_5)_3Si]_2S_{2-9}$		198
$[(CH_3)_3Si]_2SO_2$		198
$[(C_2H_5)_3Si]_2SO_2$		198
$(C_2H_5SO_2)_4Si$		198
dec above –40°		
$(C_6H_5)_3SiSLi$		46, 89
$(C_6H_5)_3SiSNa$	220°–230° (dec)	46
$(C_6H_5)_3SiSK$	233°–237°	46
$(C_6H_5)_3SiSO_2C_6H_5$		256
$[(C_6H_5)_3Si]_2S_2$	181°–182°	46
$[(CH_3)_3SiS]_3B$		10
<i>Germanium</i>		
$[RCH(CO_2H)S]_2GeO$		64
R = CH_3 or H		
$(CH_3)_3GeSLi$		189
$[(C_6H_{11})_3Ge]_2S_2$	87°	59
$(C_6H_5)_2Ge(SNa)_2 \cdot 3H_2O$	≤330°	104
$(C_6H_5)_3GeSLi$		219
$(C_6H_5)_3GeSNa$	185°–195°	104, 105
$[(C_6H_5)_3Ge]_2S_2$	171°–172°	104, 105

TABLE 7—Continued

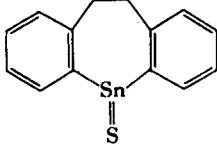
Compound	M.p. (°C)	References
<i>Germanium</i> (continued)		
$[(C_6H_5)_3Ge]_2S_3$		104, 105
$[(C_6H_5)_3GeS]_2Ge(C_6H_5)_2$	162°	104, 105
$[(C_6H_5)_3GeSCH_2]_2$	152°	69
$[(C_6H_5)_3GeSCO]_2C_6H_4$	255°–257°	69
$[(C_6H_5)_3GeSCH_2C_6H_4]_2O$		69
<i>Tin</i>		
$[(iso-C_3H_7)_3Sn]_2S_3C_2N_2$		P108
$[(n-C_4H_9)_3Sn]_2S_3C_2N_2$	(B.p. 180°/0.02 mm)	P108
$[(C_6H_{11})_3SnS(CH_2)_4OCO(CH_2)_3]_2CH_2$		P11, P42
$R'C_6H_3N_2C_2(SSnR_3)_2$		P29
$(C_6H_5)_5ClSn_2S_5$		213
$[(C_6H_5)_3SnSLi]_2$		215, 216
$(C_6H_5)_2Sn(SLi)_2$		217
		134
<i>Lead</i>		
$[(C_6H_5)_3PbSCH_2]_2$	141°–142°	69
$[(C_6H_5)_3PbS]_2C_2N_2S$	205° (dec)	69
$(C_6H_5)_3PbSLi$		220

TABLE 8

COMPOUNDS OF GENERAL FORMULA $(R_2MS)_n$

Compound	M.p. (°C)	B.p. (°C) mm	References
<i>Silicon</i>			
$[(CH_3)_2SiS]_2$	105.5° 113°	172°–173°	82, 163
$[(CH_3)_2SiS]_3$	17°–18°	153°/38	163, P54
$[(C_2H_5)_2SiS]_2$	20.1°	160°–162°/46	63
$[(C_2H_5)_2SiS]_3$			63
$[(C_2H_5S)_2SiS]_2$		296°	199
$[n-C_3H_7Si(Cl)S]_2$		261°–263°	82
$[(n-C_3H_7)_2SiS]_2$	23.5°	176°/21	82
$[(n-C_3H_7)_2SiS]_3$			82
$[(C_6H_5)_2SiS]_2$	145°–147° 163°–165°		154, P54
$[(C_6H_5)_2SiS]_3$	188°–198°		154

TABLE 8—Continued

Compound	M.p. (°C)	B.p. (°C) mm	References
<i>Germanium</i>			
$[(\text{CH}_3)_2\text{GeS}]_3$	55°	110°/1, 302°	58, 189, P53
$[(\text{iso-C}_3\text{H}_7)_2\text{GeS}]_2^a$		117°–121°/1 312°	23
$[(n\text{-C}_4\text{H}_9)_2\text{GeS}]_3$		222°–225°/1	210
$[(\text{C}_6\text{H}_5)_2\text{GeS}]_2$	203°		104
$[(\text{C}_6\text{H}_5)_2\text{GeS}]_3$	170°		104
<i>Tin</i>			
$[(\text{CH}_3)_2\text{SnS}]_3$	149°		31, 57, 92, 101, 122, 132, 155, 180, P20, P70, P79, P80, P85, P89, P101
$(\text{C}_2\text{H}_5)_2\text{SnS}$	24°	219°–221°	101
$(n\text{-C}_3\text{H}_7)_2\text{SnS}$		254°/16 (dec)	101
$(n\text{-C}_4\text{H}_9)_2\text{SnS}$		210°–214°/1	31, 43, 77, 132, 183, 203, P70, P75, P79, P80
$(n\text{-C}_8\text{H}_{17})_2\text{SnS}$			P85, P89
$(n\text{-C}_{12}\text{H}_{25})_2\text{SnS}$			P70, P80, P85, P89
$(\text{CH}_3\text{CHCl})_2\text{SnS}$	180°		259
$[(\text{CH}_3)_3\text{SiCH}_2]_2\text{SnS}$	150°–165°		224
$[(\text{C}_6\text{H}_5)_2\text{SnS}]_3$	183°		81, 135, 174, 181, 203, P20, P60, P75, P79, P80, P85, P89
$(p\text{-ClC}_6\text{H}_4)_2\text{SnS}$	179°		125
$(p\text{-BrC}_6\text{H}_4)_2\text{SnS}$			125
$(p\text{-IC}_6\text{H}_4)_2\text{SnS}$	248°		125
$(p\text{-CH}_3\text{OC}_6\text{H}_4)_2\text{SnS}$	95°		231
$(p\text{-C}_2\text{H}_5\text{OC}_6\text{H}_4)_2\text{SnS}$	127°		231
$(p\text{-C}_2\text{H}_5\text{OCOC}_6\text{H}_4)_2\text{SnS}$	142°		81
$(m\text{-CH}_3\text{C}_6\text{H}_4)_2\text{SnS}$	122°		124
$(p\text{-CH}_3\text{C}_6\text{H}_4)_2\text{SnS}$			221
$(p\text{-iso-C}_3\text{H}_7\text{C}_6\text{H}_4\text{CH}_2)_2\text{SnS}$	200°–205°		68
$(p\text{-C}_6\text{H}_5\text{C}_6\text{H}_4)_2\text{SnS}$			231
$(\alpha\text{-C}_{10}\text{H}_7)_2\text{SnS}$	215°		170
<i>Lead</i>			
$(\text{CH}_3)_2\text{PbS}$			98
$\text{CH}_3(\text{C}_2\text{H}_5)\text{PbS}$			99
$(\text{iso-C}_3\text{H}_7)_2\text{PbS}$			230
$n\text{-C}_3\text{H}_7(\text{iso-C}_4\text{H}_9)\text{PbS}$			99
$n\text{-C}_3\text{H}_7(\text{iso-C}_5\text{H}_{11})\text{PbS}$			99
$(\text{C}_6\text{H}_{11})_2\text{PbS}$			96
$[(\text{C}_6\text{H}_5)_2\text{PbS}]_3$	112°–115°		127, 144, 171, 179
$(p\text{-CH}_3\text{C}_6\text{H}_4)_2\text{PbS}$			171

^a $d_4^{20} = 1.327$; $n_D^{20} = 1.551$ (23).

TABLE 9
COMPOUNDS OF GENERAL FORMULA $[(RM)_2S_3]_n$

Compound	M.p. (°C)	B.p. (°C) mm	References
<i>Silicon</i>			
$[(CH_3Si)_2S_3]_2$	275°		83
$[(C_2H_5Si)_2S_3]_2$	140°		83
$[(n-C_3H_7Si)_2S_3]_2$	86°	210°–215°/0.2	82
$(n-C_{12}H_{25}Si)_2S_3$			25
$[(C_6H_5Si)_2S_3]_2$	216°		83
<i>Germanium</i>			
$[(C_6H_5)_2Ge]_2S_3$			42, 188
$(p-CH_3C_6H_4Ge)_2S_3$			42
$[p-(CH_3)_2NC_6H_4Ge]_2S_3$			42
$[p-(C_2H_5)_2NC_6H_4Ge]_2S_3$			42
$(\alpha-C_{10}H_7Ge)_2S_3$			42
<i>Tin</i>			
$(CH_3Sn)_2S_3$			132, 168
$(p-ClC_6H_4Sn)_2S_3$	295° (dec)		125
$(p-BrC_6H_4Sn)_2S_3$			125
$(p-IC_6H_4Sn)_2S_3$			125
$(o-CH_3C_6H_4Sn)_2S_3$			123

TABLE 10
CYCLIC COMPOUNDS INVOLVING M—S BONDS IN THE RING(S)

Compound	B.p. (°C) mm	n_D^{20}	References
<i>Silicon</i>			
$ \begin{array}{c} H_2C-CH_2 \\ \diagdown \quad \diagup \\ O-Si-S \\ \quad (CH_3)_2 \end{array} $			243
$ \begin{array}{c} H_2C-CH_2 \\ \diagdown \quad \diagup \\ O-Si-S \\ \quad (C_2H_5)_2 \end{array} $	95°/17	1.49274 ($d_{20}^4 = 1.0742$)	P55

TABLE 10—Continued

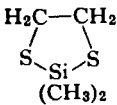
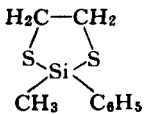
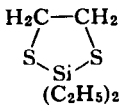
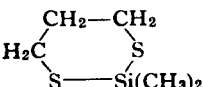
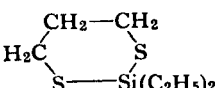
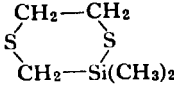
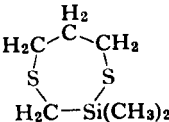
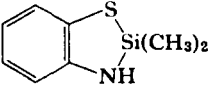
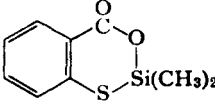
Compound	M.p. (°C)	B.p. (°C) mm	n_D^{20}	References
<i>Silicon</i> (continued)				
	8°–10°	188° 54°/2 25°–27°/12	1.5571 ($d_{20}^4 = 1.1077$)	10, 11, 249, P55
		98°/0.05	1.6180	11
		78°–80°/5	1.5350 ($d_{20}^4 = 1.0524$)	P55
	6°–8°	93°/12		247
		110°–120°/6		P55
	–17° to –14°	88°–91°/12	1.5471 ($d_{20}^4 = 1.098$)	245
		61°–63°/1		245
	95°			243, 252
	100°	158°/10		246

TABLE 10—*Continued*

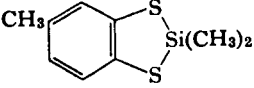
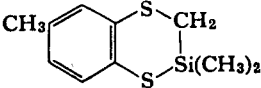
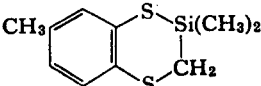
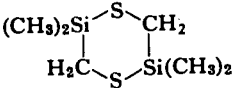
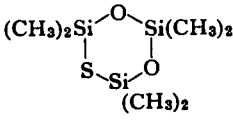
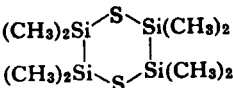
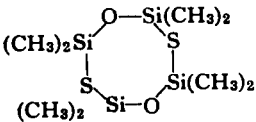
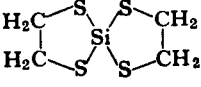
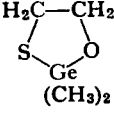
Compound	M.p. (°C)	B.p. (°C) mm	n_D^{20}	References
<i>Silicon (continued)</i>				
		108°/2	1.6142 (25°)	244, 248
				
		138°–140°/2	1.6136 (25°)	244, 248
	81°–83°			242
		172.5°		30
	111°–112°			237
	38°–42°			30
	144°			32
<i>Germanium</i>				
	–2°	64°/12		243, 250

TABLE 10—*Continued*

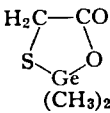
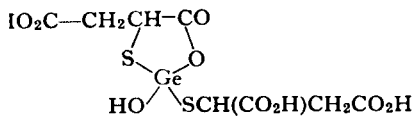
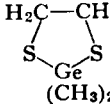
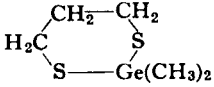
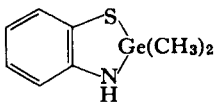
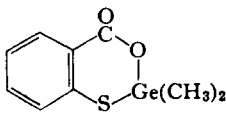
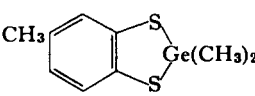
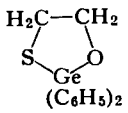
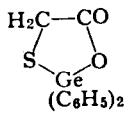
Compound	M.p. (°C)	B.p. (°C) mm	n_D^{20}	References
<i>Germanium</i> (continued)				
	129°–132°	155°/5 (sublimes)		251
				64
	13°	87°–93°/12		249
	24°–27°	103°–105°/10		247
	121°–123°			243, 252
	166°–169°	160°/3 (sublimes)		251
		120°/2	1.6381 (25°)	244, 248
	80°–81°			69
	143°–145°			69

TABLE 10—Continued

Compound	M.p. (°C)	B.p. (°C) mm	n_D^{20}	References
<i>Germanium</i> (continued)				
 $(C_6H_5)_2$	87°–88°			69
	181°			69
	165°			32, 69
 2	159°			39, 41
<i>Tin</i>				
 $(CH_3)_2$	82°–83°	113°–115°/5		11, 14, 249
 $(n-C_4H_9)_2$	59°–60°			175
 $(n-C_8H_{17})_2$				147
 $(C_6H_5)_2$	108°–109°			69, 175

TABLE 10—Continued

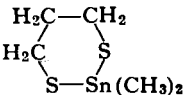
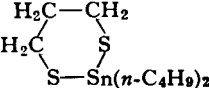
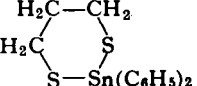
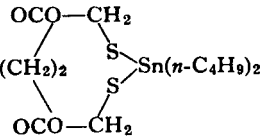
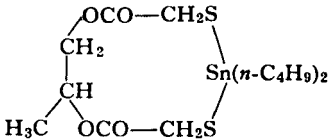
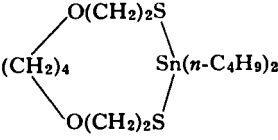
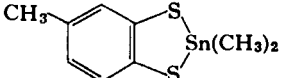
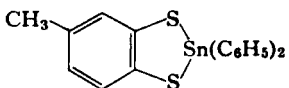
Compound	M.p. (°C)	B.p. (°C) mm	n_D^{20}	References
<i>Tin (continued)</i>				
 $\text{H}_2\text{C}-\text{CH}_2$ $\text{H}_2\text{C}-\text{S}-\text{Sn}(\text{CH}_3)_2$		113°–117°/3		247
 $\text{H}_2\text{C}-\text{CH}_2$ $\text{H}_2\text{C}-\text{S}-\text{Sn}(n\text{-C}_4\text{H}_9)_2$	63°–64°			175
 $\text{H}_2\text{C}-\text{CH}_2$ $\text{H}_2\text{C}-\text{S}-\text{Sn}(\text{C}_6\text{H}_5)_2$	103°–104°			175
 $\text{OCO}-\text{CH}_2$ $(\text{CH}_2)_2$ $\text{OCO}-\text{CH}_2$				P14
 $\text{OCO}-\text{CH}_2\text{S}$ CH_2 CH H_3C $\text{OCO}-\text{CH}_2\text{S}$				P14
 $\text{O}(\text{CH}_2)_2\text{S}$ $(\text{CH}_2)_4$ $\text{O}(\text{CH}_2)_2\text{S}$				P11, P42
 CH_3	95°–98°	158°–162°/7		244, 248
 CH_3	155°			175

TABLE 10—Continued

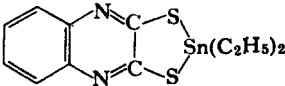
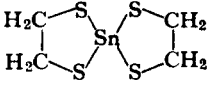
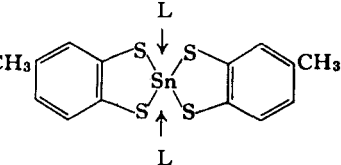
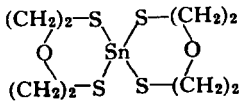
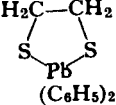
Compound	M.p. (°C)	References
<i>Tin (continued)</i>		
	218°–220°	P29
	182°	32, 175
		175
(L = pyridine or dimethylformamide)		
	124°	36
<i>Lead</i>		
	132°–133°	69

TABLE 11

POLYMERIC COMPOUNDS

Compound	M.p. (°C)	References
<i>Silicon</i>		
$(C_2H_5S)_2(SiS_2)_{21}Si(SC_2H_5)_2$		199
<i>Germanium</i>		
$[(C_6H_5)_2GeS]_x$	198°–200°	179
$[-(C_6H_5)_2GeS(CH_2)_5S-]_n \approx 80$		69

TABLE 11—Continued

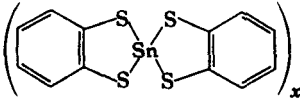
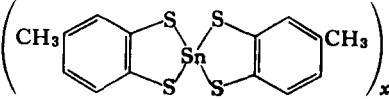
Compound	M.p. (°C)	References
<i>Germanium</i> (continued)		
$[-(\text{C}_6\text{H}_5)_2\text{GeSCH}_2\text{C}_6\text{H}_4\text{OC}_6\text{H}_4\text{CH}_2\text{S}-]_n \approx 50$		69
$(\text{Ge}[\text{S}(\text{CH}_2)_6\text{S}]_2)_x$	$\leq 300^\circ$	69
$(\text{Ge}[(\text{SCH}_2\text{C}_6\text{H}_4)_2\text{O}]_2)_x$	$\leq 300^\circ$	69
$[(\text{CH}_3)_2\text{GeSe}]_x$		190, 204
<i>Tin</i>		
$(\text{CH}_3)_2\text{ISn}[\text{SSn}(\text{CH}_3)_2]_n\text{I}$		155
		56
$[(\text{C}_6\text{H}_5)_2\text{Sn}_2\text{S}_3]_x$		208
$[(\text{C}_6\text{H}_5)_3\text{ClSn}_3\text{S}_4]_x$		213
$[(\text{C}_6\text{H}_5)_4\text{Sn}_3\text{S}_4]_x$		208
		175

TABLE 12

SELENIUM AND TELLURIUM COMPOUNDS

Compound	M.p. (°C)	B.p. (°C)/mm	References
<i>Silicon</i>			
$[(\text{CH}_3)_3\text{Si}]_2\text{Se}$		$31^\circ/2$	107, 204, 207
$[(\text{CH}_3)_2\text{SiSe}]_2$	$112^\circ\text{--}113^\circ$		204, 207
$[(\text{CH}_3)_2\text{SiSe}]_3$	$17^\circ\text{--}18^\circ$	$100^\circ/2$	204, 207
$(\text{CH}_3)_3\text{SiSeGe}(\text{CH}_3)_3$	-19° to -17°	$79^\circ/12$	190
$\text{Si}(\text{SeC}_6\text{H}_{11})_4$	94°		33
$\text{Si}(\text{SeC}_6\text{H}_5)_4$	137°		33
$\text{Si}(\text{SeC}_6\text{H}_4\text{CH}_3\text{-}p)_4$	128.5°		33
$\text{Si}(\text{SeC}_6\text{H}_4\text{Cl-}p)_4$	183°		33
$\text{Si}(\text{SeC}_6\text{H}_4\text{-}tert\text{-C}_4\text{H}_9\text{-}p)_4$	176°		33
$[(\text{CH}_3)_3\text{Si}]_2\text{Te}$		$40^\circ\text{--}42^\circ/0.25$	107

TABLE 12—Continued

Compound	M.p. (°C)	B.p. (°C)/mm	References
<i>Germanium</i>			
$[(\text{CH}_3)_3\text{Ge}]_2\text{Se}$	-12°	50°/1 94°/13	190, 204
$(\text{CH}_3)_3\text{GeSeSn}(\text{CH}_3)_3$			190
$(\text{CH}_3)_3\text{GeSeLi}$			190
$[(\text{CH}_3)_2\text{GeSe}]_3$	53°		204
$(\text{C}_6\text{H}_5)_3\text{GeSeLi}$			219
$[(\text{C}_6\text{H}_5)_3\text{Ge}]_2\text{Se}$	150°		219
$(\text{C}_6\text{H}_5)_3\text{GeSeSn}(\text{C}_6\text{H}_5)_3$	133° 145°		215, 218, 219
$(\text{C}_6\text{H}_5)_3\text{GeSePb}(\text{C}_6\text{H}_5)_3$	119°		219
$\text{Ge}(\text{Se-tert-C}_4\text{H}_9)_4$	192°–193°		33
$\text{Ge}(\text{SeC}_6\text{H}_{11})_4$	79°		33
$\text{Ge}(\text{SeC}_6\text{H}_5)_4$	119.5°		33
$\text{Ge}(\text{SeC}_6\text{H}_4\text{CH}_3\text{-}p)_4$	106°		33
$\text{Ge}(\text{SeC}_6\text{H}_4\text{-iso-C}_3\text{H}_7\text{-}p)_4$	113°		33
$\text{Ge}(\text{SeC}_6\text{H}_5\text{-tert-C}_4\text{H}_9\text{-}p)_4$	141°		33
$\text{Ge}(\text{SeC}_6\text{H}_4\text{Cl-}p)_4$	179°		33
$\text{Ge}(\text{SeC}_{10}\text{H}_7\text{-}\alpha)_4$	131°		33
$(\text{C}_6\text{H}_5)_3\text{GeTeLi}$			219
$[(\text{C}_6\text{H}_5)_3\text{Ge}]_2\text{Te}$	120°		219
$(\text{C}_6\text{H}_5)_3\text{GeTeSn}(\text{C}_6\text{H}_5)_3$	142°–146°		219
$(\text{C}_6\text{H}_5)_3\text{GeTePb}(\text{C}_6\text{H}_5)_3$	115°–117°		219
<i>Tin</i>			
$(\text{CH}_3)_3\text{SnSeC}_6\text{H}_5^a$		67°–69°/0.001	6
$[(\text{CH}_3)_3\text{Sn}]_2\text{Se}$		118°/15	132, 190
$(\text{CH}_3)_3\text{SnSe}$	120°		132, 204, 205
$(\text{CH}_3\text{Sn})_2\text{Se}_3$			132, 232
$(\text{C}_2\text{H}_5\text{Sn})_2\text{Se}_3$			232
$(n\text{-C}_4\text{H}_9)_2\text{SnSe}$			209
$(\text{C}_6\text{H}_5)_3\text{SnSeLi}$			215, 218
$[(\text{C}_6\text{H}_5)_3\text{Sn}]_2\text{Se}$	148°		204, 205
$(\text{C}_6\text{H}_5)_3\text{SnSeC}_6\text{H}_5$			203, 209
$(\text{C}_6\text{H}_5)_3\text{SnSePb}(\text{C}_6\text{H}_5)_3$	138°		220
$\text{Sn}(\text{Se-tert-C}_4\text{H}_9)_4$	190° (dec)		33
$\text{Sn}(\text{SeC}_6\text{H}_5)_4$	83.5°		33
$\text{Sn}(\text{SeC}_6\text{H}_4\text{CH}_3\text{-}p)_4$	119°		33
$\text{Sn}(\text{SeC}_6\text{H}_4\text{Cl-}p)_4$	201.5°		33
$\text{Sn}(\text{SeC}_6\text{H}_4\text{-tert-C}_4\text{H}_9\text{-}p)_4$	132°		33
$(\text{C}_6\text{H}_5)_3\text{SnTeLi}$			215, 218
$((\text{C}_6\text{H}_5)_3\text{Sn})_2\text{Te}$	148°		215

TABLE 12—Continued

Compound	M.p. (°C)	B.p. (°C)/mm	References
<i>Lead</i>			
(CH ₃) ₃ PbSeCH ₃ ^b		75°/3	P91, P102
(CH ₃) ₃ PbSeC ₆ H ₅ ^c			P102
(C ₆ H ₅) ₃ PbSeLi			220
[(C ₆ H ₅) ₃ Pb] ₂ Se	101°		220
(C ₆ H ₅) ₃ PbTeLi			220
[(C ₆ H ₅) ₃ Pb] ₂ Te	128°–129°		220

^a $d_4^{20} = 1.650$; $n_D^{20} = 1.6119$ (6).

^b $d = {}_4^{20} 2.42$ (P91, P102).

^c $d_4^{20} = 2.60$ (P102).

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The Structural Chemistry of Organo- Transition Metal Complexes: Some Recent Developments

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I. Introduction	93
II. The Bonding of Cyclic Conjugated Ligands to Transition Metal Ions	94
A. π -Cyclopentadienyl Complexes.	94
B. Other Arene-Metal Complexes	98
III. Conjugated Diolefin Complexes	100
IV. Three-Membered Carbon Skeletons	105
A. Allyl Complexes	105
B. Cyclopropane Complexes.	112
V. Organometallic Molecules Derived from Acetylenes	114
A. Complexes Containing Nonpolymerized Acetylene Ligands	116
B. Complexes Containing the Metallocyclopentadiene and Related Systems	120
C. Complexes Containing other Simple Metallo-Substituted Ring Systems	122
VI. Alkyl and Fluoroalkyl Complexes of Transition Metal Ions	125
VII. Metal Carbonyls and Substituted Carbonyls	128
References	131

I

INTRODUCTION

The growth in activity, over the last decade, in the general area of organo-metallic chemistry of transition metal ions is due, to a considerable extent, to the discovery and characterization of ferrocene. While most methods of structural analysis have been used in attempts to elucidate the nature of the bonding in these molecules, their complexity is often such that only diffraction methods provide unequivocal information relating to molecular stereochemistry; this review deals almost exclusively with such data but we have

not felt that a description of the principles of crystal structure analysis would be appropriate except where some comment is needed on the accuracy of determination of molecular parameters. We have also found it necessary to restrict our survey to certain classes of organometallic molecules and in so doing have omitted, for reasons of space rather than of prejudice, discussions of such important topics as organometallic complexes of sulfur, nitrosyl, and simple olefinic ligands.

II

THE BONDING OF CYCLIC CONJUGATED LIGANDS TO TRANSITION METAL IONS

A. π -Cyclopentadienyl Complexes

The general nature of the bonding in bis(π -cyclopentadienyl) complexes of transition metal ions is now reasonably well established (156), although even in these relatively simple molecules a number of questions remain to be

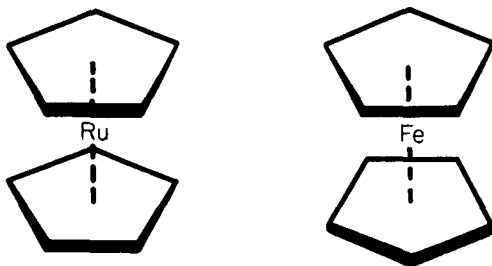


FIG. 1. Stereochemistry of ruthenocene and ferrocene.

answered, at least in a quantitative way. The first is concerned with the differences in molecular symmetry between the isoelectronic molecules, ferrocene and ruthenocene. Ferrocene, in the crystalline state, apparently has D_{5d} symmetry (65) while that of ruthenocene is D_{5h} (82) (Fig. 1). An explanation for this difference was initially based on the view that the larger radius of the ruthenium ion allowed the eclipsed conformation, in so far as the nonbonded interannular carbon-carbon distances in ruthenocene are close to the van der Waals diameter of carbon whereas the eclipsed conformation for ferrocene would give contacts considerably less than 3.5 Å. However, since the barrier to rotation of the ligands about the metal-to-ring

axes is small, it is possible that structures observed in the solid state result from constraints imposed by inter- rather than intramolecular interactions. This point was first elaborated by Edwards *et al.* (68), since which time studies of other structures have become available. The structure of diferrocenyl (99, 109) is such that the π -cyclopentadienyl rings are mutually oriented in a conformation almost exactly intermediate between the staggered and eclipsed arrangements. The structures of bis(π -indenyl) iron (148), (π -C₅H₄SO₂Cl)₂Fe (141), (π -C₅H₄COC₆H₅)₂Fe (142, 143) and a variety of acyl ferrocene compounds (142–144) have the strictly staggered conformation. In several other ferrocene derivatives, the conformation of the substituted π -cyclopentadienyl ligands is obviously influenced by the nature of the interannular bridging groups. Thus, in 1,1'-tetramethylethyleneferrocene (130), the π -cyclopentadienyl ligands are inclined so as to make an angle of 156.8° between the planes of the rings which are rotated about their fivefold axes through an angle of only 9°–10° with respect to one another—that is the ligands are very close to an eclipsed configuration. A similar situation is found in another bridged ferrocene derivative; α -keto-1,1'-trimethyleneferrocene is 11.8° away from the eclipsed configuration but the angle between the planes of the five-membered rings is now 171.2° (95). Other substituted ferrocene complexes whose structures have recently been reported include diethylferrocene (97) and bis(chloro)ferrocene (98). The ruthenocene derivatives that have been examined—bis(acetyl)ruthenocene (148) and bis(π -indenyl)ruthenium (151)—have the π -C₅H₅ ligands in the strictly eclipsed form. The structural analysis of ferrocenyl ruthenocenyl ketone, C₅H₅FeC₅H₄COC₅H₄RuC₅H₅ (135), shows that the cyclopentadienyl rings of *both* the ferrocene and the ruthenocene portions of the molecule have the same relative configuration, which is about intermediate between the staggered and eclipsed configurations.

A recent report of a structural investigation of ferrocene dicarboxylic acid (121b) indicates that the π -cyclopentadienyl rings in this complex are only 1.6° from the strictly eclipsed conformation.

Osmocene is crystallographically isomorphous (92) with ruthenocene and therefore may reasonably be assumed to have D_{5h} symmetry.

A wide range of π -cyclopentadienyl molecules of the first-, second-, and third-row metals are such that there is a considerable dihedral angle between the individual cyclopentadienyl rings; these molecules are typified by the π -cyclopentadienyl metal halides and hydrides.

Although only preliminary data have been obtained for (π -C₅H₅)₂TiCl₂

(133) and $(\pi\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$ (22), the stereochemistry of the metal atoms is likely to be similar to that in $(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}_2\text{Al}(\text{C}_2\text{H}_5)_2$ (36, 119) where the π -cyclopentadienyl rings are nonparallel and the titanium ion can be regarded as tetrahedrally coordinated by two chlorine atoms and two "effectively unidentate" π -cyclopentadienyl ligands.

The first structure reported of a tris(π -cyclopentadienyl) compound is that of $(\pi\text{-C}_5\text{H}_5)_3\text{UCl}$ (158) where the three π -cyclopentadienyl anions and the chlorine are again arranged so as to give a pseudotetrahedral configuration around the uranium. In terms of the usual description of the π -cyclopentadienyl anion as a terdentate ligand, the uranium is ten-coordinate.

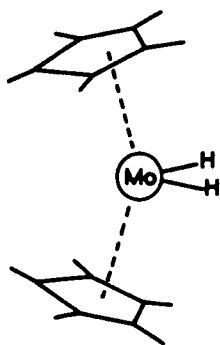
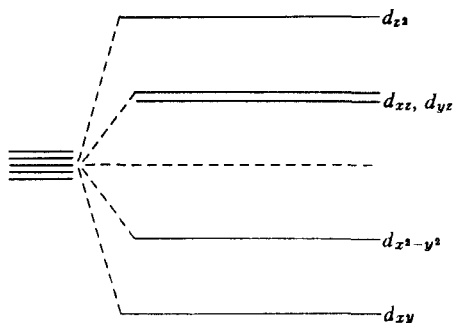


FIG. 2. Molecular structure of $(\pi\text{-C}_5\text{H}_5)_2\text{MoH}_2$.

Only one structure of a π -cyclopentadienyl metal hydride complex has been determined (74). The structures of several di- π -cyclopentadienyl hydrides, of general formula $(\pi\text{-C}_5\text{H}_5)_2\text{MH}_x$ ($x = 1, 2$ or 3) were originally suggested to be trigonal bipyramidal in which parallel cyclopentadienyl rings occupy axial positions (79). If the cyclopentadienyl rings were considered as terdentate ligands, the structure of the trihydride complex would be related to that of the $(\text{ReH}_9)^{2-}$ ion (1). The nuclear magnetic resonance spectra of the trihydride tantalum and tungsten species showed, however, that the structures were more likely to be distorted trigonal bipyramids since the proton spectrum occurred as an A_2B grouping (77). The suggested nonlinearity of the metal-to-ring axes was confirmed by an X-ray crystal analysis of $(\pi\text{-C}_5\text{H}_5)_2\text{MoH}_2$ (Fig. 2), which showed the dihedral angle between the π -cyclopentadienyl rings to be $34^\circ \pm 1^\circ$ (74). This observation is in keeping with the conclusions of Ballhausen and Dahl (14), who showed that within the framework of molecular orbital theory the overlap of metal and cyclopentadienyl orbitals was not much reduced by tilting the ligands

with respect to one another, provided that the dihedral angle between the rings did not exceed 45° . Presumably the reason why the structure of $(\pi\text{-C}_5\text{H}_5)_2\text{MoH}_2$ adopts its particular configuration rather than the symmetrical $(\text{ReH}_9)^{2-}$ or $[\text{Nd}(\text{H}_2\text{O})_9]^{3+}$ structure lies in the fact that in such a structure as the $(\text{ReH}_9)^{2-}$ the cyclopentadienyl-metal distance would need to be large, with a consequent decrease of overlap, to accommodate the sterically active hydrogens.

The large dihedral angle between the cyclopentadienyl ligands in $(\pi\text{-C}_5\text{H}_5)_2\text{MoH}_2$ prompts an additional question about the bonding in π -cyclopentadienyl complexes of low symmetry. Although the precise arrangement of the energy levels in molecules such as ferrocene remains a question of debate, there is general agreement that most of the metal-cyclopentadienyl bonding arises from the overlap of the degenerate d_{yz} and d_{xz} orbitals of the metal with the doubly degenerate high-lying filled molecular orbitals on the ligand. Now if we have a situation where the ligands *trans* to the cyclopentadienyl ligand do not confer a cylindrically symmetric environment around the metal ion, the degeneracy of the metal d orbitals is removed, which may lead to the situation in which the fivefold symmetry of the $\pi\text{-C}_5\text{H}_5$ ring is lost (17). The splitting of the metal d orbitals in complexes of low symmetry containing the cyclopentadienyl ligand can be conveniently examined by a consideration of the structure of tricarbonyl- π -cyclopentadienylethylmolybdenum (16). Randic (125) calculated the d orbital energies, within a crystal-field approximation, by idealizing the molecular geometry so that although the symmetry of the molecule is only C_s , the effective symmetry for d^1 and d^2 configurations is C_{4v} . The energy level diagram is then



However, the results are based on an incorrect assumption relating to bond angles in the complex. Randic assumed that the angles, θ' and θ'' , between

the z axis and the fivefold and fourfold axes of the two organic fragments were 30° and 109.5° , respectively; the actual values are 31° and 149° , the latter being an average result. A recalculation of the perturbed energy levels with these parameters indicates that the position of the d_{z^2} orbital relative to d_{xz} and d_{yz} is strongly dependent on the Randic ratio G_2/G_4 , where

$$G_n = \int_0^\infty R^2(r) \frac{r^n}{r^{n+1}} r^2 dr$$

Moreover, the distortion of the ligand set $[(\text{CO})_3\text{Et}]$ from C_{4v} symmetry produces a splitting of d_{xz} and d_{yz} and it would seem impossible to attempt to locate the relative positions of the three energy levels, except that $d_{xz} \approx d_{z^2} > d_{yz} > d_{x^2-y^2} > d_{xy}$. A naive molecular orbital treatment along the lines of the discussion of the detailed geometry of $\text{Mn}_2(\text{CO})_{10}$ (18) is in good agreement with this ordering. In molecular orbital terms, the distortion of the $(\text{CO})_3\text{Et}$ moiety from C_{4v} symmetry leads to the situation where the d_{xz}/p_x and d_{yz}/p_y hybrids, used for bonding to the cyclopentadienyl e^\pm orbitals, have differing amounts of d and p character. The question which remains for further data to comment upon is how large the difference in the bond lengths of the cyclopentadienyl ligand in asymmetric complexes is. As Bennett *et al.* commented originally (17), an independent spectroscopic check that the results do not arise from systematic errors in the X-ray data is needed. For the particular case of second- and third-row transition metal complexes, the realization of carbon-carbon bond lengths with a standard deviation of approximately 0.01 \AA is difficult and yet must be achieved if any individual result is to be interpreted in detail. The arguments put forward so far rely on the fact that a pattern of bond length distortions has emerged for a number of molecules but this is clearly not a completely satisfactory state of affairs.

B. Other Arene-Metal Complexes

A number of these complexes have been studied and they are listed in Table I.

A great deal of the available data about these molecules have centered around the question of the bonding in dibenzenechromium. Jellinek (93, 94) suggested that the molecule had only D_{3h} symmetry corresponding to the localization of a Kekulé form in the coordinated ligands. Cotton *et al.* (40),

TABLE I

Molecule	References
$(\pi\text{-C}_6\text{H}_6)_3\text{V}$	Fischer <i>et al.</i> (71, 152)
$(\pi\text{-C}_6\text{H}_6)_2\text{Cr}$	Cotton <i>et al.</i> (40); Jellinek (94); Ibers (90); Jellinek (93); Weiss and Fischer (152)
$(\pi\text{-C}_6\text{H}_6)_2\text{Mo}$	Weiss and Fischer (152)
$(\pi\text{-CH}_3\text{C}_6\text{H}_5)_2\text{Cr}^+\text{I}^-$	Strarovskii and Struchov (139, 140)
$\pi\text{-C}_6\text{H}_6\text{Cr}(\text{CO})_3$	Bailey and Dahl (10); Corradini and Allegra (4, 37, 38)
$[\pi\text{-C}_6(\text{CH}_3)_6]\text{Cr}(\text{CO})_3$	Bailey and Dahl (8)
$[\pi\text{-C}_6\text{H}_5\text{—Cr}(\text{CO})_3]_2$	Corradini and Allegra (39); Allegra (5)
$\pi\text{-C}_{14}\text{H}_{10}\text{Cr}(\text{CO})_3$	Deusche and Hoppe (55)
1-exo- $\text{C}_6\text{H}_5\text{—C}_7\text{H}_7\text{Cr}(\text{CO})_3$	Barkie <i>et al.</i> (15)
$\text{C}_7\text{H}_8\text{Mo}(\text{CO})_3$	Dunitz and Pauling (66)
$[\text{C}_6\text{H}_6\text{PdAl}_2\text{Cl}_7]_2$	Allegra <i>et al.</i> (6)

on the basis of new diffraction data, found that, within the limits of error of their determination, the coordinated benzene rings had sixfold symmetry; Ibers (90) carried out a statistical survey of the Cotton *et al.* data and supported the finding that the molecule has D_{6h} symmetry. No threefold distortion of the cyclic ligand has been discovered in $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ (9) or in $\text{C}_6(\text{CH}_3)_6\text{Cr}(\text{CO})_3$ (8). There is an apparent twofold distortion in the hexamethylbenzene complex which Bailey and Dahl (8) believe to be a property of the free ligand. This seems unlikely. The need for a low-temperature diffractometer analysis of the bond lengths in several of these molecules remains, although the D_{6h} symmetry of dibenzenechromium is almost certain to be confirmed.

All the bis(arene)metal complexes are believed to be of D_{6h} , rather than D_{6d} , symmetry (cf. the cyclopentadienyl situation). Similarly all arene-metal tricarbonyls whose structures have been determined have the carbonyl ligands *trans* to the center of a carbon-carbon bond in the benzene skeleton although no statistically significant distortion in the intraring bond lengths is found, or indeed, is to be expected in complexes of this stoichiometry. It is interesting to note that in the structure of $\text{C}_7\text{H}_8\text{Mo}(\text{CO})_3$, the carbonyl groups may each be *trans* to a localized olefinic carbon-carbon bond (66). The completion of the rather more accurate analysis of the structure of 1-exo- $\text{C}_6\text{H}_5\text{—C}_7\text{H}_7\text{Cr}(\text{CO})_3$ (15) may clarify this point. In the phenanthrenechromium tricarbonyl structure (55) the aromatic ligand is positioned so that the region of maximum π -electron density in the free

ligand is closest to the metal—the structure, unfortunately, is of limited accuracy.

One of the more unexpected bis(benzene)–transition metal structures that has been reported is that of Allegra *et al.* (6) in which two palladium atoms are sandwiched between a pair of benzene rings (Fig. 3).

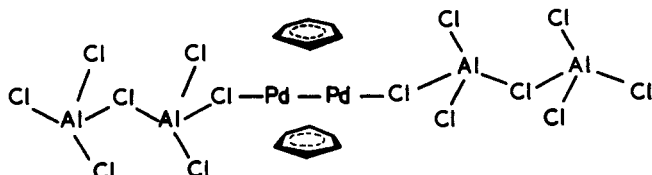


FIG. 3. The structure of $(\text{C}_6\text{H}_6\text{PdAl}_2\text{Cl}_7)_2$.

One π -cycloheptatrienyl compound has been examined. The crystal structure of $(\pi\text{-C}_7\text{H}_7) \text{V} (\pi\text{-C}_5\text{H}_5)$ shows the $\pi\text{-C}_7\text{H}_7$ to be delocalized and confirms the expectation that the geometry of such complexes is governed by constancy of metal–carbon distance rather than by a constant metal–plane-of-ring distance (69).

III

CONJUGATED DIOLEFIN COMPLEXES

Structural investigation of conjugated diolefin complexes falls under several separate headings (Table II).

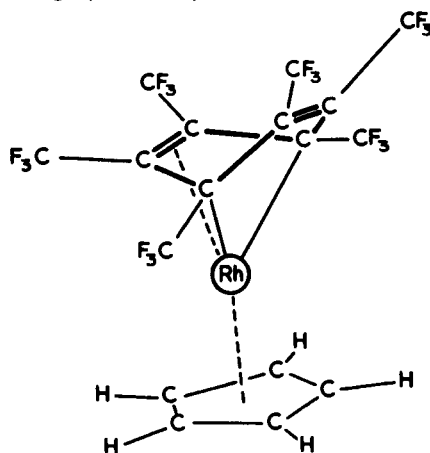


FIG. 4. The stereochemistry of π -cyclopentadienyl-hexakis(trifluoromethyl)benzene rhodium, showing the bending of the benzene ligand.

TABLE II
CONJUGATED DIOLEFIN COMPLEXES

<i>Butadiene complexes</i>	
$(cis-C_4H_6)Fe(CO)_3$	Mills and Robinson (115, 116)
$(cis-C_4H_6)_2RhCl$	Porri <i>et al.</i> (123)
<i>Cyclopentadiene complexes</i>	
$\pi-C_5H_5Co(C_5H_5C_6H_5)$	Churchill and Mason (25, 29)
$\pi-C_5H_5Co(C_5H_5COC_6H_5)$	Churchill (30)
$\pi-C_5H_5Re(CH_3)_2(C_5H_5CH_3)$	Alcock (3)
<i>Cyclopentadienone complexes</i>	
$\pi-C_5H_5Co[(CH_3)_4C_5O]$	Dahl and Smith (47)
$\pi-C_5H_5Co[(CF_3)_4C_5O]$	Gerloch and Mason (73)
$(CO)_3Fe[(CF_3)_4C_5O]$	Bailey <i>et al.</i> (12); Bailey and Mason (13)
<i>Cyclohexadiene complexes</i>	
$(C_6F_8)Fe(CO)_3$	Churchill and Mason (27, 34)
$C_{10}H_{18}Fe(CO)_3$	Robson and Truter (128)
<i>Hexakis(trifluoromethyl)benzene complex</i>	
$(\pi-C_5H_5)Rh[(CF_3)_6C_6]$	Churchill and Mason (26, 34a)
<i>Cycloheptatrienone complexes</i>	
$(C_7H_6O)Fe(CO)_3$	Dodge (60)
$[C_7(C_6H_5)_3H_3O]Fe(CO)_3$	Smith and Dahl (137)
<i>Cyclooctatetraene complexes</i>	
$C_8H_8Fe(CO)_3$	Dickens and Lipscomb (56, 57)
$C_8H_8[Fe(CO)_3]_2$	Dickens and Lipscomb (56, 58)
<i>Cyclobutadiene complexes</i>	
$[(CH_3)_4C_4]NiCl_2 \cdot C_6H_6$	Dunitz <i>et al.</i> (67)
$[(C_6H_5)_4C_4]Fe(CO)_3$	Dodge and Schomaker (61, 63)

The classification represented in Table II is perhaps at first sight surprising; it is, in fact, only in the last 2 years or so that it has been realized that a number of aromatic cyclic ligands behave towards the addition to a metal ion as a substituted butadiene. The point is nicely illustrated by the structure of π -cyclopentadienylhexakis(trifluoromethyl)benzenerhodium (26, 34a) in which a nonplanar benzene nucleus is stabilized (Fig. 4). Only four atoms of the substituted six-membered ring are involved in the formation of the metal-ligand bond. As such, the bonding of the cyclic

ligand to the metal is identical with that observed in, for example, cyclopentadiene complexes (3, 25, 29, 30) and cyclohexadiene systems (27); the free cyclic ligand in all these cases is planar but in the organometallic complex has a dihedral form in which the angular nonplanarity may have a value of up to 48° or so.

The first clue to the nature of the bonding in these types of molecules came from a comparison of π -cyclopentadienyltetramethylcyclopentadienonecobalt (47) and its perfluoromethylcyclopentadienone analog (73); the dihedral angle of the substituted cyclopentadienone in the tetramethyl case is much less than in the perfluoromethyl example. In simple valence-bond terms, which have, as we shall see, only a conceptual value, the nonplanarity

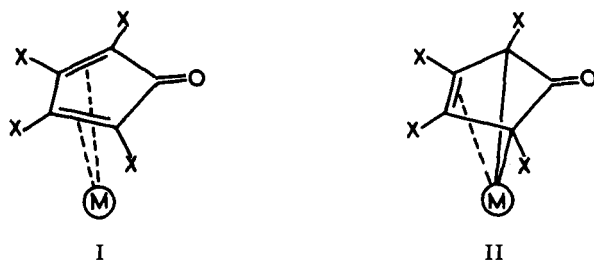


FIG. 5. The cyclopentadienone ligand. (I) The π -bonded structure (II) The σ - and π -bonded structure.

of the cyclopentadienone ligand is explained by postulating the formation of *localized* metal-ligand bonds (Fig. 5).

Clearly the conformation of the substituted cyclopentadienone ligands shows that the presence of the electronegative $-\text{CF}_3$ groups encourages the formation of metal-ligand σ bonds. Within this simple formulation, the oxidation state of the metal differs by +2 in the structures (I) and (II) but it must be recognized that this is simply a formalism and should not be interpreted literally any more than one understands the situation in ferrocene in which the iron is given an oxidation state of zero or +2 depending on whether the ligand is regarded as an anion or a radical.

According to a molecular orbital theory of the electron distribution in a cyclic ligand, the possible role of structure (II) may be measured by the atom-electron localization energy. A valid correlation of ring conformation with electron density must be restricted to rings of roughly equal geometry so that it is instructive to compare the electron localization energies in cyclopentadienone and cyclopentadiene (Fig. 6).

The localization energies for electrophilic attack are smaller for cyclopentadiene than for cyclopentadienone. The distortions from planarity of the diene ligands in π -cyclopentadienyl-1-phenylcyclopentadienecobalt (29), π -cyclopentadienyl-1-benzoylcyclopentadienecobalt (30), and dimethyl- π -cyclopentadienylmethylcyclopentadienerhenium (3) are 37° , 37° , and 38° , respectively; while the values with cyclopentadienone ligands are 10° in π -C₅H₅Co[(CH₃)₄C₅O] and 20° in π -C₅H₅Co[(CF₃)₄C₅O] and (CO)₃Fe[(CF₃)₄C₅O].

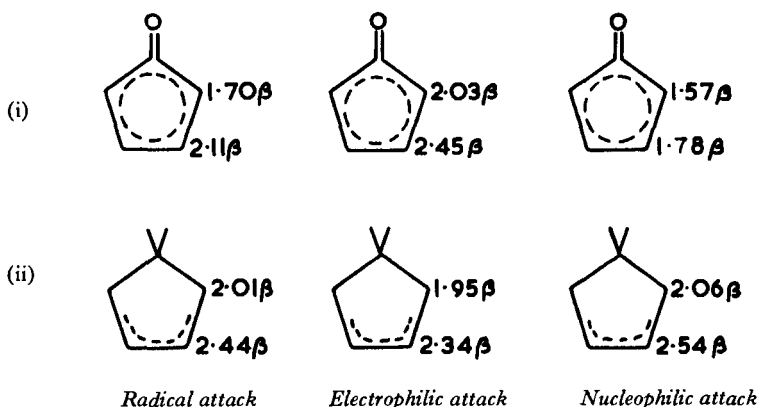


FIG. 6. Atom localization energies in (i) cyclopentadienone and (ii) cyclopentadiene.

It is worth-while examining the relationship of the simple valence-bond description to that which emerges from molecular orbital theory. If the four $p\pi$ orbitals of the *cis*-butadiene residue are labeled A to D , they form the basis for molecular orbitals of symmetries $2A_2$ and $2B_2$ which, neglecting overlap, take the form

$$\begin{aligned}
 b_2(1) &= \frac{1}{\sqrt{1+\lambda^2}} \{A + D + \lambda(B + C)\} & \alpha + 1.6\beta \\
 b_2(2) &= \frac{1}{\sqrt{1+\lambda^2}} \{\lambda(A + D) - (B + C)\} & \alpha - 0.6\beta \\
 a_2(1) &= \frac{1}{\sqrt{1+\mu^2}} \{(A - D) + \mu(B - C)\} & \alpha + 0.6\beta \\
 a_2(2) &= \frac{1}{\sqrt{1+\mu^2}} \{\mu(A - D) - (B - C)\} & \alpha - 1.6\beta
 \end{aligned}$$

The bonding molecular orbitals of (I) span B_2 and A_2 and the ligand contribution to the molecular orbitals arises from $b_2(1)$ and $a_2(1)$. Formula (I) does not allow explicitly for the back-donation process whereas the σ - π -bonded structure (II) has bonding molecular orbitals which span $2B_2$ and A_2 where, besides $b_2(1)$ and $a_2(1)$, the ligand combination $b_2(2)$ is involved.

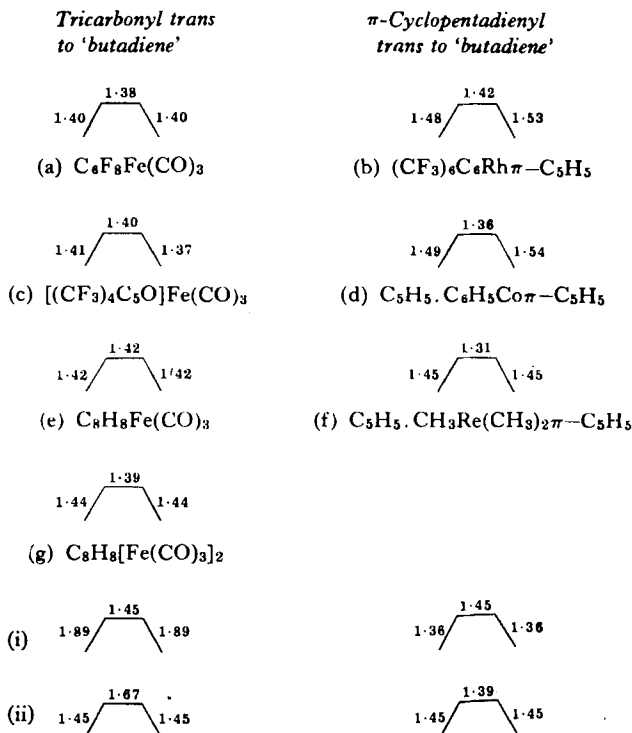


FIG. 7. Bond lengths in substituted butadiene complexes and Hückel (total) bond orders and calculated bond lengths (Å) in (i) the ground and (ii) the excited states of butadiene.

Thus the formulations (I) and (II) do not imply fundamental differences in the electronic structure; rather there is a smooth transition between the two schemes as $b_2(2)$ contributes increasingly to the bonding (102). The contribution which this level makes depends on its energy and what is particularly important about cyclopentadienone is its very low lying anti-bonding orbital.

Clearly, however, the amount of, say, back-donation into a cyclic ligand will reflect the nature of the ligands *trans* to itself. We can predict that if

the π -cyclopentadienyl ligand is *trans*, its relatively poor accepting properties will guarantee that considerable back-donation to the butadiene fragment will occur; conversely, if the strongly π -accepting carbonyls are *trans* to the butadiene fragment, a good deal less electron density will accumulate in the lowest antibonding orbital of butadiene. With these comments in mind, the bond lengths in the butadiene fragments of seven structures can be examined.

The results in Fig. 7 are interpretable in terms of the π -bond orders of butadiene in its ground and excited states.

The bond lengths in the substituted butadiene fragment when there is a *trans*- π -C₅H₅ ligand demonstrate unequivocally the population of the lowest antibonding orbital of butadiene *via* back-donation from the metal. This back-donation is altogether less when there are carbonyl groups *trans* to the butadiene, the C—C bond lengths now being roughly equal, a situation explained by approximately equal weights of the ground and excited state bond lengths as in (i) and (ii). (In valence-bond language the π -C₅H₅ ligand stabilizes the contribution of the σ - π structure.)

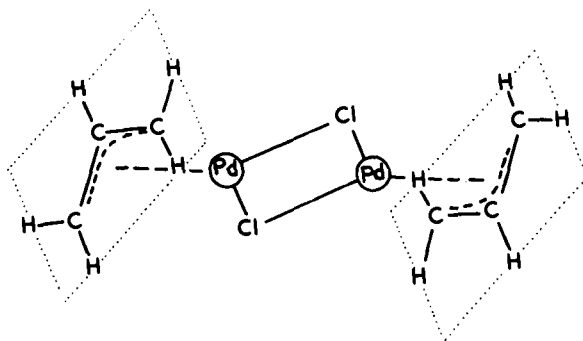
IV

THREE-MEMBERED CARBON SKELETONS

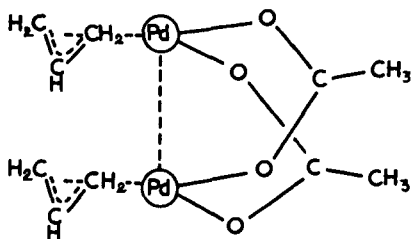
A. Allyl Complexes

The chemistry of allyl complexes has recently been reviewed in this series (78) but already a number of structural analyses have been completed which allow further comments to be made on the bonding in these molecules.

The first π -allyl transition metal complex to be examined by crystallographic methods was the dimeric π -allylpalladium chloride. Preliminary investigations (129, 132) were followed by three-dimensional analyses at room temperature (121) and -140°C (136). The molecule has strict C_i symmetry with the three carbon and five hydrogen atoms of the allyl ligand forming a plane which is oriented at $111.5^\circ \pm 0.9^\circ$ to the plane containing the PdCl₂Pd bridge system (Fig. 8). The average C—C bond length is 1.376 Å (e.s.d. 0.015 Å) which is surprisingly close to the free ligand value. The reaction of π -allylpalladium chloride with silver acetate gives π -allylpalladium acetate, the structure of which is again based on a dimer but without C_i symmetry. The molecular stereochemistry (Fig. 9) (28) is

FIG. 8. π -allyl palladium-chloride.

remarkably similar to that of cupric acetate dihydrate (150), a fact which may not be unimportant in relation to certain catalytic systems involving π -allylpalladium acetate and small traces of cupric ions.

FIG. 9. The stereochemistry of π -allyl-palladium acetate.

Bis(methallyl)nickel has been shown, by a two-dimensional X-ray analysis, to be a sandwich compound with the nickel atom at the center of symmetry of two methallyl ligands (Fig. 10) (59). The methallyl ligand itself is substantially nonplanar, the methyl groups being displaced approximately 0.5 Å out of the allyl plane *toward* the metal.

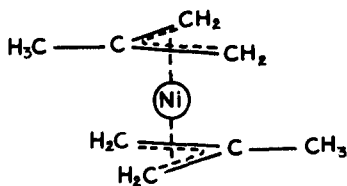


FIG. 10. The structure of bis(methallyl)nickel.

The reaction of sodium cyclopentadienide with tetramethylcyclobutadienenickel dichloride (45) yields a cyclobutenyl complex (120). Only three atoms of the cyclobutenyl ring are involved in the metal-ligand bond, the fourth being bent away from the metal by 24.9° (Fig. 11). The intraring angle at this atom is only 80.1° compared with $\sim 91.5^\circ$ ($\pm 3^\circ$) for the other

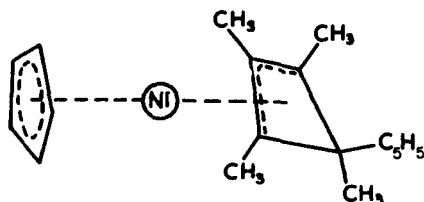


FIG. 11. The structure of 1-*exo*-cyclopentadienyltetramethylcyclobutenyl- π -cyclopentadienyl nickel.

three carbon atoms. Each angle is therefore decreased from the value expected on the basis of its nominal hybridization state by approximately 30° . The methyl groups of the π -allyl system are displaced by 0.13–0.21 Å away from the nickel, a situation reminiscent of that in tetramethylcyclobutadienenickel dichloride (67).

It seems strange that, in the formation of this cyclobutenyl complex, as in the preparation of substituted cyclopentadiene complexes (72, 80) [for

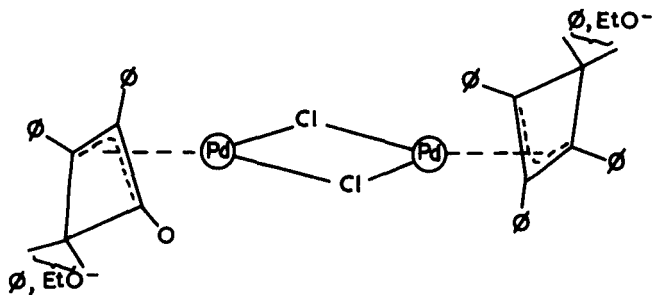


FIG. 12. The isomers of ethoxytetraphenylcyclobutenylpalladium chloride.

example, $(\pi\text{-C}_5\text{H}_5)_2\text{Co}^+ + \text{LiR} \rightarrow (\pi\text{-C}_5\text{H}_5)\text{Co}(\text{C}_5\text{H}_5\text{R}) + \text{Li}^+$], the final product is an *exo*-substituted ring (25, 29, 30). It seems therefore that the reaction is not initiated via a nucleophilic attack at the metal, followed by transfer to the ligand, but rather by direct attack on the ligand. The formation of the *exo*-substituted ring may be assumed to be the result of the steric shielding of the inner side of the ring. Structural analyses have also been completed of the *endo*- and *exo*-ethoxy isomers of dimeric ethoxytetraphenylcyclobutenylpalladium chloride (Fig. 12) (54).

The tendency for palladium to form π -allyl complexes rather than linking to a conjugated diene system has been well documented (126) in the reactions of butadiene, and its derivatives, with sodium chloropalladite in various alcoholic solutions, where π -(alkoxy)butenyl systems are formed. This tendency continues with larger conjugated systems, as is evidenced by a

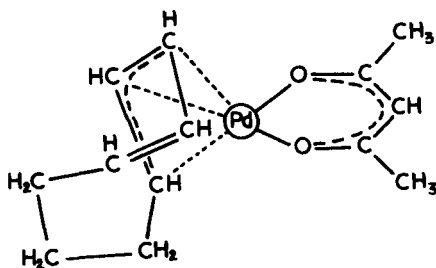


FIG. 13. The structure of cyclooctadienyl-palladium acetylacetonate.

structural determination of cyclooctadienylpalladium acetylacetonate (Fig. 13) (31, 127). Only three atoms of the dienyl ligand are involved in bonding to the palladium atom, the average Pd—C bond length being $2.11 \pm 0.01 \text{ \AA}$; the remaining unsaturated carbon atoms are at 2.93 and 3.93 \AA , respectively, from the metal.

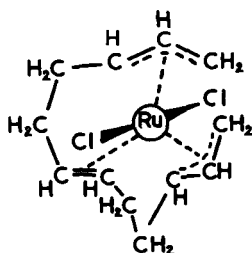


FIG. 14. The complex of ruthenium with trimerized butadiene, showing the terminal allyl groups.

The suggestion by Wilke (155) that dodeca-2,6,10-triene-1,12-dienyl-nickel, an α - ω diallyl complex, might well be an intermediate in the trimerization of butadiene to *trans,trans,trans*-cyclododeca-1,5,9-triene with nickel-containing catalysts has been indirectly substantiated by recent work. Thus butadiene reacts with ruthenium trichloride in 2-methoxyethanol to give a complex $[\text{RuCl}_2(\text{C}_4\text{H}_6)_3]$ which has been shown to be a dodeca-2,6,10-triene-1,12-dienyl complex (Fig. 14) (108). π -Allyl transition

metal complexes have also been noted in polymerization reactions of acetylenes to give substituted benzene. The complex $\text{Co}_2(\text{CO})_4(\text{C}_2\text{HBU}^t)_2\text{C}_2\text{H}_2$ is a diallyl complex (Fig. 15) (117). The related complex, $\text{Co}_2(\text{CO})_4(\text{C}_2\text{HBU}^t)_3$, liberates the otherwise inaccessible 1,2,4-tri-*tert*-butylbenzene on reaction with bromine (106). The intermediate formation of these diallyls thus seems to provide a general method for obtaining highly substituted benzenes.

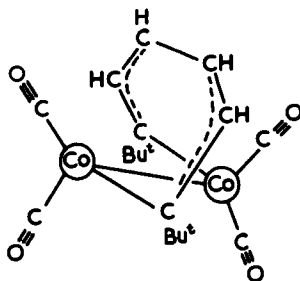


FIG. 15. The structure of $\text{Co}_2(\text{CO})_4(\text{C}_2\text{HBU}^t)_2\text{C}_2\text{H}_2$.

A number of authors have commented upon the conversion of π -allylic complexes into σ -allylic species in such solvents as dimethyl sulfoxide. Nuclear magnetic resonance studies of the methallylpalladium chloride–triphenylphosphine system (124) led to suggestions relating to the structures

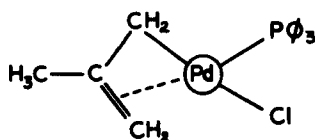


FIG. 16. The structure of a σ - and π -allyl complex.

of intermediates in the π - σ -allyl conversion. The formulation in Fig. 16 has recently been confirmed by an X-ray analysis (112); the molecular geometry is shown in Fig. 17. The dihedral angle between the allyl C_3 plane and that defined by the palladium, phosphorus, and chlorine atoms is 116° ; the methallyl ligand itself is significantly nonplanar, the methyl group being displaced 0.5 \AA out of the plane C1-C2-C3 towards the metal. As such it is similar to the situation in the more symmetrical bis(methallyl)nickel complex (59) and it will be of interest to examine the bond lengths in this complex in some detail to discover whether there is evidence for some localized metal–carbon bonding.

The available structural data on allyl complexes are summarized in Table III so far as the conformation of the allyl ligand with respect to the remaining atoms in the coordination sphere is concerned.

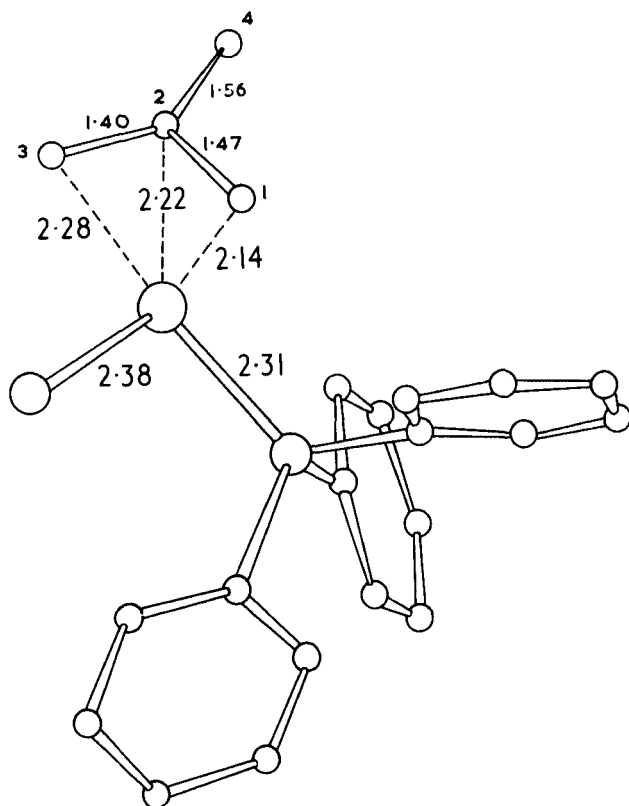


FIG. 17. The molecular geometry of $(\text{C}_3\text{H}_4\text{Me})\text{PdP}(\text{C}_6\text{H}_5)_3\text{Cl}$.

The nonorthogonality of the allyl ligand to the other groups in several of these structures has recently been discussed by Kettle and Mason (103). A consideration of the various metal-ligand overlap integrals in allylpalladium complexes predicts dihedral angles of approximately 110° , a value in reasonable agreement with experiment. Figure 18 shows that there are two extreme conformations of the allyl ligand, corresponding to dihedral angles of 90° and 180° , with respect to the plane containing the metal and remaining ligands. In orientation (I) the geometry is such that a line drawn from, say, the palladium atom to the midpoint of the line joining the two equivalent

TABLE III
ALLYL COMPLEXES

Complex	Dihedral angle	References
$[\pi\text{-C}_3\text{H}_5\text{PdCl}]_2$	111.5° between allyls and PdCl_2Pd plane	136
$[\pi\text{-C}_3\text{H}_5\text{PdCH}_3\text{COO}]_2$	117° (average) between allyl and PdO_2 planes	28
$[\text{C}_8\text{H}_{11}\text{Pd acac}]$	121° between allyl and PdO_2 plane	31, 34c
$[\text{endo-EtOC}_4(\text{C}_6\text{H}_5)_4\text{PdCl}]_2$	95° between allyl and PdCl_2Pd plane	54
$[\text{exo-EtOC}_4(\text{C}_6\text{H}_5)_4\text{PdCl}]_2$	95° between allyl and PdCl_2Pd Plane	54
$(\text{C}_3\text{H}_4\text{Me})\text{PdP}(\text{C}_6\text{H}_5)_3\text{Cl}$	116° between allyl plane and PdPCl plane but methallyl ligand nonplanar	112
$(\text{C}_5\text{H}_5\text{Me}_4\text{C}_4)\text{Ni}(\pi\text{-C}_5\text{H}_5)$	1° between allyl and $\pi\text{-C}_5\text{H}_5$ planes	120
$(\pi\text{-C}_3\text{H}_4\text{Me})_2\text{Ni}(\pi\text{-C}_5\text{H}_5)$	0° between allyl planes but methallyl groups nonplanar	59
$[\pi\text{-CH}_2\text{C}(\text{CO}_2\text{Et})\text{CH}_2\text{NiBr}]_2$	109° between allyls and NiBr_2Ni plane	34b

carbon atoms of the allyl group is perpendicular to the plane defined by the carbon atoms of the allyl group whereas in orientation (II) the atoms are coplanar with the metal. The three π molecular orbitals of the allyl ligand, in the Hückel approximation, are of b_1 (twice; energies $\alpha \pm \sqrt{2}\beta$) and of a_2 symmetry of the C_{2v} group. The overlap of metal orbitals with the anti-bonding ligand molecular orbital can be shown by explicit calculation to be very small. Table IV shows the significant overlap integrals which palladium

TABLE IV
OVERLAP INTEGRALS

	Allyl orbital		χ (dihedral angle)
	$b_1(1)$	a_2	
Energy	$\alpha + \sqrt{2}\beta$	α	
Orientation I	0.426	0.365	90°
Palladium orbital	d_{z^2}	d_{xz}	
Orientation II	0.285	0.166	180°
Palladium orbital	d_{yz}	d_{xy}	

orbitals may use in bonding to the allyl ligand. The dihedral angle at which the total bonding energy is maximized can be shown to be given by

$$\chi = [180^\circ - \tan^{-1}(S_I/S_{II})^2]$$

and the dihedral angles predicted separately from the $b_1(1)$ and a_2 interactions are 114° and 102°. If all the other, much smaller, overlap integrals are

included in the calculation, the $b_1(1)$ and a_2 interactions are maximized at dihedral angles of 112° and 102° .

These considerations are, in fact, capable of generalization to a wide range of metal-ligand interactions. Only in very symmetrical structures, such as $(\pi\text{-C}_5\text{H}_5)_2\text{Fe}$, $(\pi\text{-C}_6\text{H}_6)_2\text{Cr}$, and $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_3$ does one find the planes of the two sets of ligands to be strictly parallel. For example, the dihedral

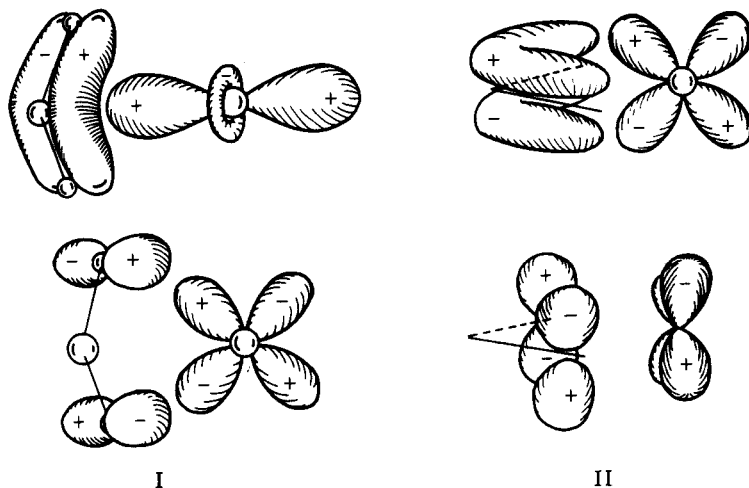


FIG. 18. The molecular orbital scheme for the bonding of the π -allyl system. (I) The perpendicular and (II) the horizontal bonding situation.

angle between the planes containing the three carbonyl carbon atoms and the butadiene fragment in tricarbonyloctafluorocyclohexa-1,3-diene iron is 111° (27, 34), while that between the $\pi\text{-C}_5\text{H}_5$ ring and the substituted butadiene fragment in $\pi\text{-C}_5\text{H}_5\text{Rh}[(\text{CF}_3)_6\text{C}_6]$ is 99° (26, 34a). The corresponding values in $\pi\text{-C}_5\text{H}_5\text{Co}(\text{C}_5\text{H}_5\text{C}_6\text{H}_5)$ (29) and $(\text{CO})_3\text{Fe}[(\text{CF}_3)_4\text{C}_5\text{O}]$ (12, 13) are 95° and 96.6° , respectively. One might mention that the structure of Zeise's salt remains to be determined in an accurate way; certain features of the wide-line magnetic resonance spectra of Zeise's salt remain to be clarified (110) and a knowledge of the orthogonality or otherwise of the ethylene ligand to the PdCl_3 plane would be valuable.

B. Cyclopropane Complexes

Platinum chloride dissolved in acetic anhydride reacts (147) with cyclopropane to form a brown polymer $[(\text{C}_3\text{H}_6)\text{PtCl}_2]_n$, which may be converted,

using pyridine, to the monomeric complex $[(C_3H_6)PtCl_2(py)_2]$ (Fig. 19). Both these complexes react with aqueous potassium cyanide to give cyclopropane, this reaction together with other data, leading to their formulation (2) as complexes containing the trimethyleneplatinum(IV) moiety. In warm

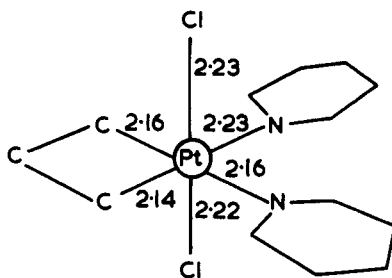


FIG. 19. Molecular dimensions in a cyclopropane-platinum complex.

benzene, the pyridine complex slowly changes to a yellow "isomer." It is surprising that these complexes have not, until recently, been examined by X-ray methods. The recrystallization of the yellow isomer from a chloro-

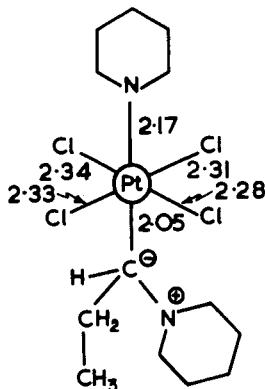


FIG. 20. An "ylide" complex of platinum, showing some bond lengths.

form-carbon tetrachloride solution affords beautiful yellow crystals whose structure has now been completely elucidated (Fig. 20) (75).

The stabilization of the "ylide" structure is quite remarkable. On thermal decomposition, the complex yields propene quantitatively. Ylides have been regarded as intermediates in elimination reactions of organic molecules, and phosphonium ylides are involved in the Wittig reaction. The structure

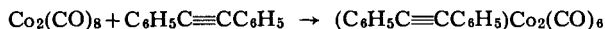
represented in Fig. 20 suggests that these and other highly reactive species, such as the carbenes and benzyne, may be stabilized by coordination with a transition metal; there seems no reason to doubt that the cyclopropane reactions open up a new area of preparative and structural organometallic chemistry.

V

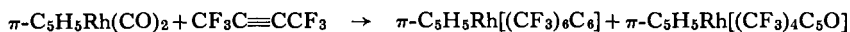
ORGANOMETALLIC MOLECULES DERIVED FROM ACETYLENES

The products formed by the reaction of acetylenes with transition metal carbonyls may be widely differing in their chemical nature (89). Further, the interaction of a metal carbonyl with an acetylene may result in the formation of a large number of species. For reasons of convenience alone, these products may be classified into the following groups which are determined by *how far* the reaction has proceeded:

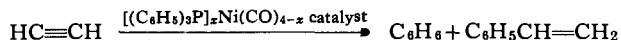
- (i) Complexes in which one or more of the acetylenes has become bonded to the metal and is still identifiable as such. One, or more, of the carbonyl groups of the parent molecule may have been lost, e.g.,



- (ii) Complexes in which the acetylene ligands attached to the metal have become linked together. The metal may act as a hetero atom in facilitating ring-closure of the organic system formed; also, carbonyl groups may be transferred from the metal into the organic system, e.g.,



- (iii) Organic molecules based on the polymerization of the acetylenes, possibly with insertion of carbonyl groups, e.g.,



It is difficult to predict, with any preciseness, exactly how far a given reaction will go and whether there will be a single product or a variety of products. One general rule appears to be useful, however; the reaction of a metal carbonyl with a liquid acetylene, obviating the need for a solvent, tends to give a complex with a high ratio of acetylene molecules to metal ions.

Figure 21 shows a number of products which on the basis of the above classification might be expected to result from the interaction of a mono-nuclear metal carbonyl with an acetylene.

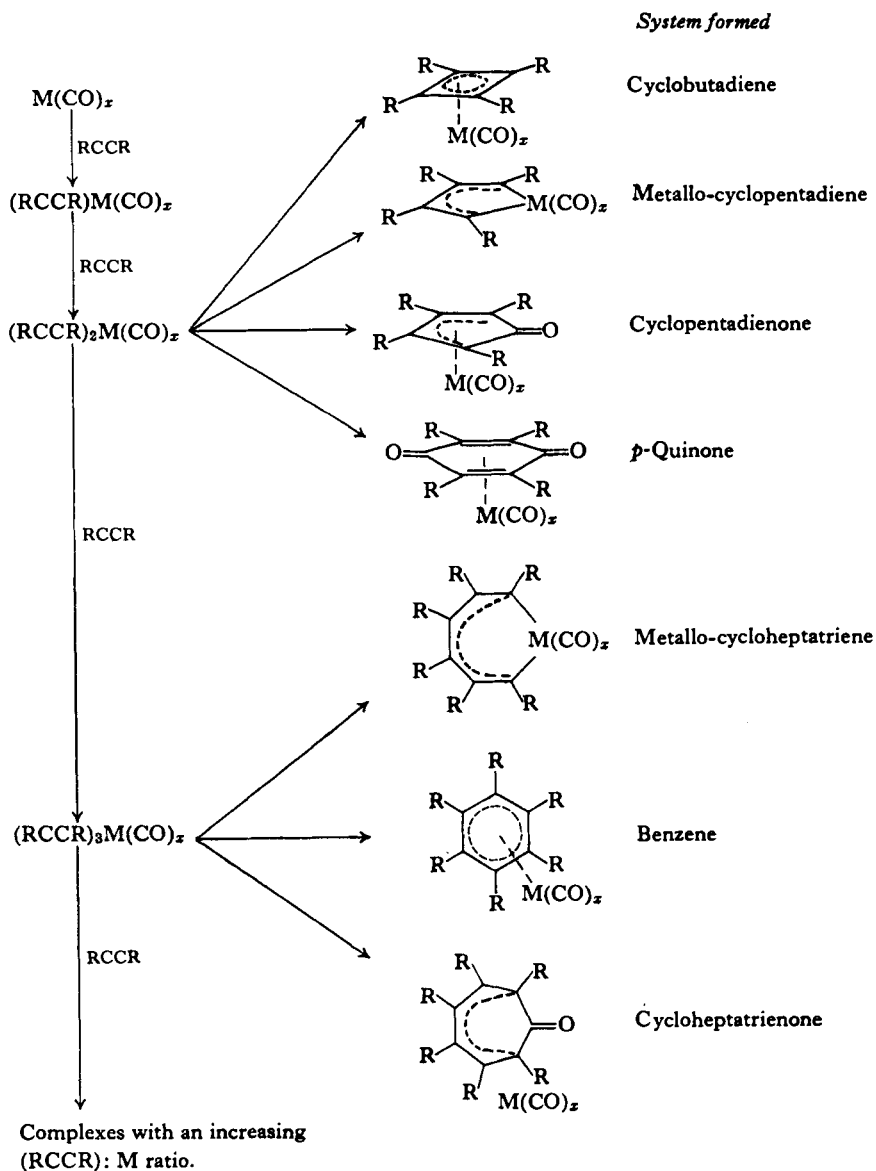


FIG. 21. The reactions of an acetylene with a transition metal carbonyl, showing some of the systems that may be produced.

When the reactant is a polynuclear metal carbonyl, the number, and diversity, of the possible products is greatly increased; the tendency for gross rearrangement becomes greater owing to the possibility of ligand transfer from one metal center to another.

The following survey of acetylene complexes is again arranged, as far as possible, in terms of how far the reaction has proceeded. Some of the possible products, such as cyclobutadiene, cyclopentadienone, benzene, and cycloheptatrienone complexes have been discussed earlier and are therefore omitted from the present section.

A. Complexes Containing Nonpolymerized Acetylene Ligands

The large majority of complexes falling under this heading are those in which the acetylene ligand acts as a bridging group between two (or more)

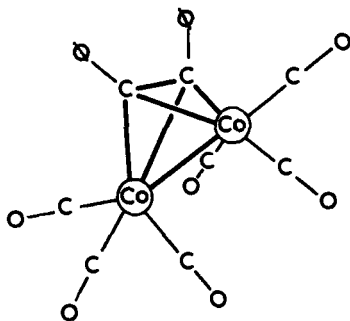
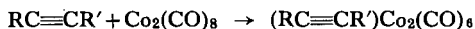


FIG. 22. The structure of the diphenylacetylene complex formed from dicobaltoctacarbonyl.

metal centers. Dicobalt octacarbonyl appears to have two cobalt atoms at an ideal distance to be bridged by an acetylene since the reaction



appears to be quite general (81, 138). The product with $\text{R}, \text{R}' = \text{C}_6\text{H}_5$, has been examined crystallographically (134) and found to have the structure shown in Fig. 22.

The cobalt-cobalt distance is 2.47 Å compared with that of 2.52 Å in $\text{Co}_2(\text{CO})_8$ itself (145); the two acetylenic carbons lie in a line almost (88°) at right angles to the metal-metal bond and the molecule has approximate C_{2v} symmetry if the phenyl groups are ignored. A very similar structure (Fig. 23) is observed in the cyclic acetylenic complex, perfluorocyclohex-1-yn-3-ene-

dicobalt hexacarbonyl, which results from the defluorination of perfluorocyclohexa-1,3-diene on reaction with dicobalt octacarbonyl (11, 13). The metal-metal bond length in this complex is 2.47 Å, again somewhat shorter than that in $\text{Co}_2(\text{CO})_8$.

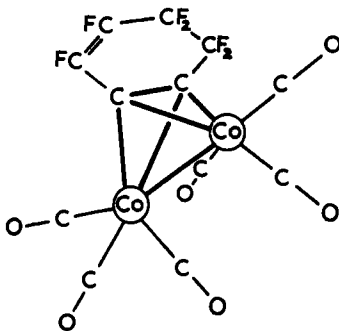


FIG. 23. The structure of perfluorocyclohex-1-en-3-yn-1-yl dicobalt hexacarbonyl.

In general, the reaction of an iron carbonyl with an acetylene tends to proceed to the stage at which the acetylenes link to form a *complex* organo-metallic molecule. However, one of the products from the reaction of triiron dodecacarbonyl with diphenylacetylene (88) has the empirical formula

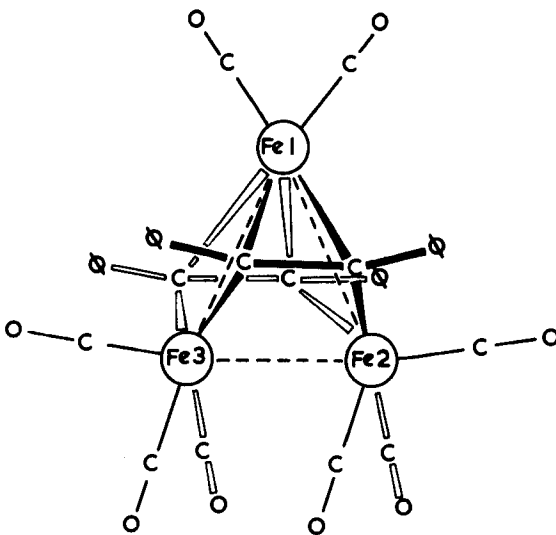
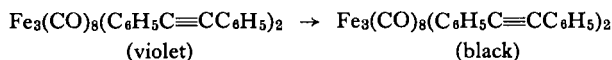


FIG. 24. The violet isomer of $\text{Fe}_3(\text{CO})_9(\text{C}_6\text{H}_5\text{CCC}_6\text{H}_5)_2$.

$\text{Fe}_3(\text{CO})_8(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)_2$. An X-ray analysis (64) of this violet-colored form shows the molecule to contain two separate bridging diphenylacetylene ligands each of which straddles all three iron atoms; the iron-iron bond lengths are 2.47, 2.46, and 2.59 Å (Fig. 24). The average formal acetylenic bond length of 1.39 Å implies that the ligands are best regarded as part of a multicenter bonding system.

A preference for the acetylene-iron carbonyl system to go further along the reaction path rather than just forming an acetylene-substituted carbonyl complex is illustrated by the facile rearrangement in boiling benzene,



As discussed later, the black isomer contains the stable ferracyclopentadiene moiety.

The bridging potentiality of an acetylene group attains its maximum in the structure of $\text{Co}_4(\text{CO})_{10}(\text{EtC}\equiv\text{CEt})$ (48) in which the diethylacetylene

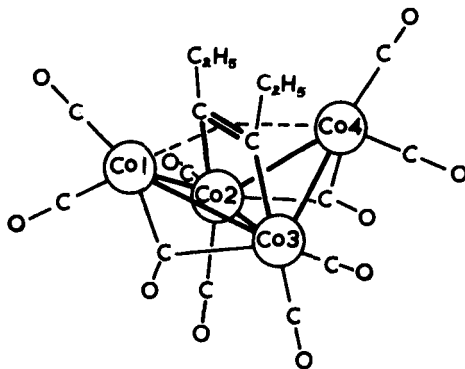


FIG. 25. The complex formed from diethylacetylene and $\text{Co}_4(\text{CO})_{12}$.

ligand is bonded to all four cobalt atoms via a σ -bonded bridge between two of the cobalt atoms and μ bonds to the remaining metal ions (Fig. 25). Again the five cobalt-cobalt bond lengths show significant differences from one another with values of 2.45, 2.43, 2.44, 2.42, and 2.55 Å (all ± 0.005 Å). The structure of $\text{Fe}_3(\text{CO})_9(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$, prepared from diphenylacetylene and diironnonacarbonyl has been reported (21) as containing an isosceles triangle of iron atoms, each having two carbonyl groups coplanar with the iron atoms; the remaining three carbonyl groups, one on each atom, are perpendicular to the defined plane and all *cis*. The diphenylacetylene

ligand is bonded in a delocalized manner and is situated *trans* to the three carbonyls.

Another novel structure which is conveniently included here is that formed by the reaction of nickelocene with bis(methylcarboxylato)-

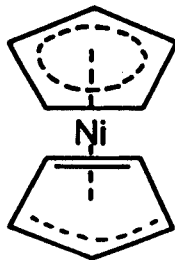


FIG. 26. A hypothetical structure for nickelocene, indicating how the molecule often reacts.

acetylene. Nickelocene, formally a 20-electron complex (two over the 18) often reacts as though it were as formulated in Fig. 26. With the acetylene $\text{MeCO}_2\text{C}\equiv\text{CCO}_2\text{Me}$, nickelocene forms the complex $\pi\text{-C}_5\text{H}_5\text{Ni}[\text{C}_5\text{H}_5\text{MeCO}_2\text{CCCO}_2\text{Me}]$ in which the acetylene molecule

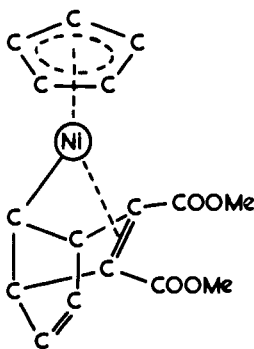


FIG. 27. The product from the reaction of nickelocene with bis-(methylcarboxylato)-acetylene.

has maintained its identity (although not, of course, bonded in the customary manner to the metal) (57) (Fig. 27). The final product is easily envisaged if the reaction is considered as the addition of an acetylene across the 1,3-position of a π -allyl fragment.

Preliminary crystallographic data are available on the nickel-acetylene complex, $(\pi\text{-C}_5\text{H}_5)_2\text{Ni}_2(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$ (118).

B. Complexes Containing the Metallocyclopentadiene and Related Systems

Once two acetylene molecules have become associated with a single metal atom, a possible reaction product is that formed by the inclusion of the

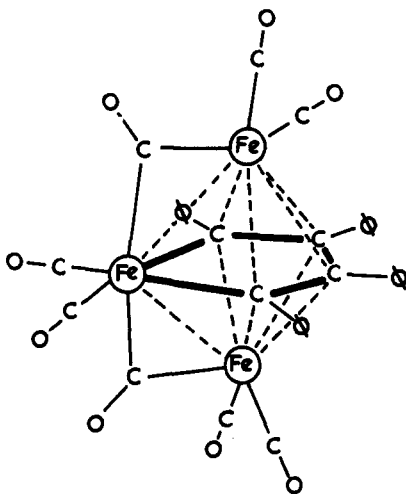


FIG. 28. The black isomer of $\text{Fe}_3(\text{CO})_8(\text{C}_6\text{H}_5\text{CCC}_6\text{H}_5)_2$.

metal atom to form a five-membered heterocyclic ring system. The ferracyclopentadiene system is observed in the black isomer of $\text{Fe}_3(\text{CO})_8(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)_2$ in which an iron carbonyl group is bonded to the π system of the planar ferracyclopentadiene ring on either side of the ring (Fig. 28).

Similar ferracyclopentadiene systems are also produced by indirect routes. For example, the reaction of dimethylacetylene with alkaline solutions of iron carbonyl hydride produces $\text{H}_2\text{Fe}_2(\text{CO})_8(\text{MeC}\equiv\text{CMe})$ in which a ferracyclopentadiene ring has been formed from one molecule of acetylene and two carbonyl groups (86, 87) (Fig. 29). One of the products of the reaction of triiron dodecacarbonyl with diphenylacetylene is $\text{Fe}_2(\text{CO})_6(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$ in which the ferracyclopentadiene ring is

formed through the part-utilization of one of the phenyl groups in the original diphenylacetylene ligand (149) (Fig. 30).

The reaction of osmium carbonyl with 2,3-dimethylbutadiene leads to the loss of two hydrogen atoms from the ligand and the formation of an osma-

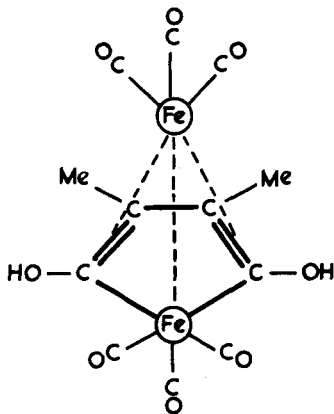


FIG. 29. The structure of $\text{H}_2\text{Fe}_2(\text{CO})_8(\text{MeCCMe})$.

cyclopentadiene system (62) (Fig. 31). The osmium atom in the π -bonded $\text{Os}(\text{CO})_3$ group is in an approximately octahedral environment (considering the osmium atom as forming two μ bonds with the osmacyclopentadiene

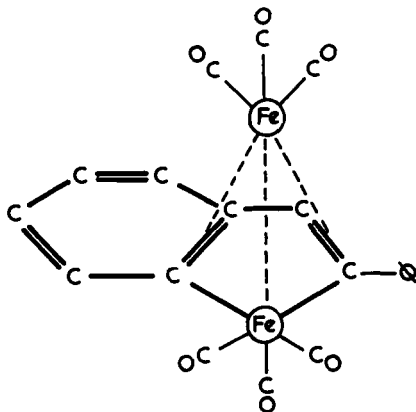


FIG. 30. The structure of $\text{Fe}_2(\text{CO})_8(\text{C}_6\text{H}_5\text{CCC}_6\text{H}_5)$; note how the original diphenylacetylene molecule has been utilized in forming a ferracyclopentadiene ligand.

ring). However, the corresponding iron atom in $\text{H}_2\text{Fe}_2(\text{CO})_8(\text{MeC}\equiv\text{CMe})$ is in a trigonal prismatic environment—the $\text{Fe}(\text{CO})_3$ group is rotated by 60° relative to the $\text{Os}(\text{CO})_3$ group. This is precisely the opposite situation to that encountered in ferrocene, ruthenocene, and osmocene and to the present reviewers the result is difficult to explain in steric or electronic terms. Moreover, the high symmetry of the complexes in what is an altogether less symmetrical environment in the crystal may obviate explanations based on the role of crystal packing.

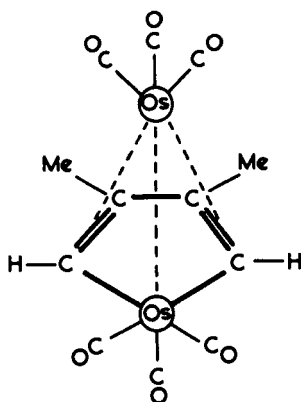


FIG. 31. The structure of an osmacyclopentadiene complex.

C. Complexes Containing other Simple Metallo-Substituted Ring Systems

The products of the reaction of acetylene with triiron dodecacarbonyl (153) include two isomers of formula $\text{Fe}_2(\text{CO})_6(\text{C}_2\text{H}_2)_3$. One of these has

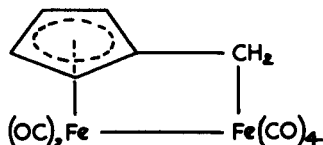


FIG. 32. An iron-alkyl complex formed from acetylene and $\text{Fe}_3(\text{CO})_{12}$.

the structure shown in Fig. 32 (113) and is considered in the section on alkyls. The other contains a 5-methylene-1,2-diferracyclohepta-3,6-diene system (Fig. 33) (122).

The reaction of monophenylacetylene with triiron dodecarbonyl produces, *inter alia*, a complex of empirical formula $\text{Fe}_2(\text{CO})_6(\text{C}_6\text{H}_5\text{C}\equiv\text{CH})_3$

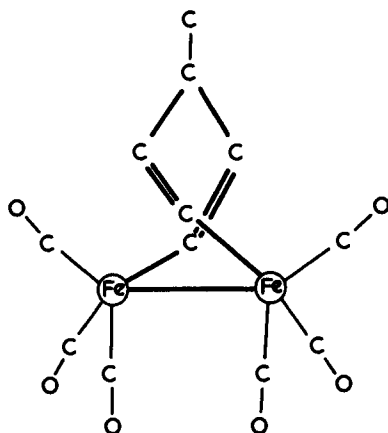


FIG. 33. $(\text{C}_2\text{H}_2)_3\text{Fe}_2(\text{CO})_6$; a molecule containing a seven-membered heterocyclic ring.

whose structure (104) is not related to those found for the simple acetylene complexes described above. The Fe—Fe bond length is 2.50 Å and the $\text{Fe}(\text{CO})_2$ group is bound to the rest of the molecule via a simple μ bond and

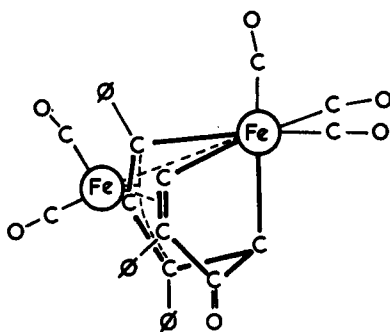


FIG. 34. The bonding in $\text{Fe}_2(\text{CO})_6(\text{C}_6\text{H}_5\text{CCCH})_3$.

a metal- π -allyl interaction (Fig. 34). This complex undergoes a series of quite interesting reactions: Although stable at room temperature, it decomposes near its melting point to give *sym*-triphenylbenzene; in boiling benzene it is converted into the two isomers of triphenyltroponeiron

tricarbonyl [see, for example, (137)]; triphenylphosphine liberates triphenyltropone from the complex.

A final class of complexes which might be considered in this section are those formed by the polymerization of acetylenes with dicobaltoctacarbonyl. The complex $\text{Co}_2(\text{CO})_4(\text{C}_2\text{HBu}^t)_2(\text{C}_2\text{H}_2)$ is a diallyl complex (117) containing a 1,2-dicobaltacycloocta-3,6-dien-5,8-diyl ligand and has been discussed earlier.

1. Duroquinone Complexes

Although bis(duroquinone)nickel is known and believed, on the basis of spectroscopic work, to contain square planar nickel (131), the only definitive structural work on *p*-quinone complexes yet reported is that on 1,5-cyclooctadieneduroquinonenickel (76). The molecule consists of a nickel atom

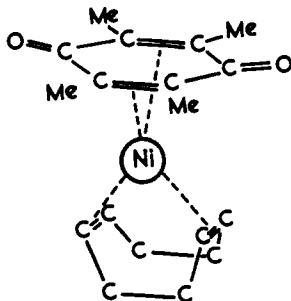


FIG. 35. The structure of a duroquinone-nickel complex.

sandwiched between a cyclooctadiene and a duroquinone ligand. If the nickel is presumed to form μ bonds to the centers of the available π bonds, it is essentially in a tetrahedral environment. The duroquinone ligand appears to be bonded via two μ bonds to the metal but there is probably a little interaction with the carbon atoms of the carbonyl groups since each of these groups is bent away from the metal by some 6° (Fig. 35); this is a situation familiar in substituted butadiene complexes (*vide supra*).

2. A σ -Bonded Lactone Complex

Although $\text{Co}_2(\text{CO})_8$ normally interacts with acetylene to give $\text{Co}_2(\text{CO})_6\text{HC}\equiv\text{CH}$, more energetic conditions favor the formation of $\text{Co}_2(\text{CO})_9\text{HC}\equiv\text{CH}$, which is found to contain a lactone group and a bent metal-metal bond (114) (Fig. 36). It is of some interest to note that this structural analysis led to the correct prediction of the structure of dicobaltoctacarbonyl, the analysis of which was completed some years later (145).

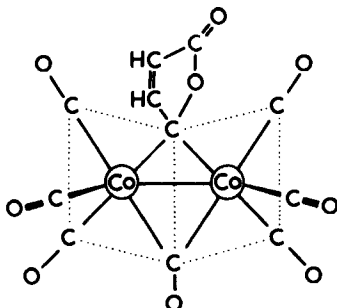


FIG. 36. $\text{Co}_2(\text{CO})_9(\text{HCCH})$; complex containing a σ -bonded lactone.

VI

ALKYL AND FLUOROALKYL COMPLEXES OF TRANSITION METAL IONS

The structures of several alkyl and fluoroalkyl complexes of transition metal ions have been determined during the past 2 years, following discussions of the nature of metal-carbon (alkyl) bonds by a number of authors (24, 91). The three metal-alkyl structures examined in detail are $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{C}_2\text{H}_5$ (16), $\pi\text{-C}_5\text{H}_5\text{Re}(\text{CH}_3)_2(\text{C}_5\text{H}_5\text{CH}_3)$ (3), and $(\text{OC})_2\text{Fe}(\pi\text{-C}_5\text{H}_4)\text{-CH}_2\text{Fe}(\text{CO})_4$ (113). The large differences in thermodynamic and kinetic stability of metal-fluoroalkyl and metal-alkyl complexes has also led to an examination of the geometries of $\pi\text{-C}_5\text{H}_5\text{Rh}(\text{CO})(\text{C}_2\text{F}_5)\text{I}$ (32, 33) and $\text{K}_3[\text{Co}(\text{CN})_5\text{CF}_2\text{CF}_2\text{H}]$ (111). The molybdenum-ethyl complex can be regarded as one in which the transition metal ion is seven-coordinate with, at first sight, the so-called 3:4 arrangement described by Dahl and Sutton (50) for the structure of $\text{Fe}_3(\text{CO})_9\text{Se}_2$. However, the ligand set $(\text{CO})_3\text{C}_2\text{H}_5$ does not have even approximate C_{4v} symmetry so that a more convenient and accurate description of the molecular stereochemistry is 3:2,2. The length of the metal-carbon (C_2H_5) bond is identical with the sum of the carbon (sp^3) radius and that of the molybdenum radius deduced from the length of the Mo—Mo bond in the "supersandwich," $\{\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\}_2$ (157). According to Cotton and Wing (44), the molybdenum-ethyl bond length is what is to be expected on the basis of an inferred molybdenum carbon bond order-bond length curve. However, the validity of this comment depends critically upon the proposition that the radius of the metal atom is insensitive to

changes in both its oxidation state and coordination number (hybridization). In $\pi\text{-C}_5\text{H}_5\text{Re}(\text{CH}_3)_2(\text{C}_5\text{H}_5\text{CH}_3)$ the rhenium-carbon (methyl) bonds average 2.25 Å, which suggests a rhenium covalent radius of 1.48 Å (3). Cotton (42) suggested a radius of 1.3 Å for rhenium(IV) from a study of the bond lengths in rhenium-chloro complexes, so that clearly some caution is needed in discussing metal-carbon, bond order-bond length relations. In $(\text{OC})_2\text{Fe}(\pi\text{-C}_5\text{H}_4)\text{-CH}_2\text{Fe}(\text{CO})_4$ (113) the $\text{Fe-C}(\text{H}_2)$ bond length is 2.12 Å compared with an average $\text{Fe-C}(\text{C}_5\text{H}_4)$ bond length of 2.06 Å and of 2.05 Å in ferrocene itself; unfortunately, a detailed discussion of these values is not possible since the σ -bond radius of octahedral Fe^{2+} varies enormously among the known complexes. The lengths of the platinum-methyl bonds in the structure of trimethyl(acetylacetonyl)-2:2'-bipyridylplatinum are not unusual (146) although this molecular analysis was of considerable interest in establishing, for the first time, an example of a β -diketone acting as a unidentate ligand [see also Figgis *et al.* (70)].

Of the fluoroalkyl complexes which have been studied, the high symmetry of the $\{\text{Co}(\text{CN})_5\text{CF}_2\text{CF}_2\text{H}\}^{3-}$ ion allows a more straightforward interpretation of the bond lengths (111) than in the example of $\pi\text{-C}_5\text{H}_5\text{Rh}(\text{CO})(\text{C}_2\text{F}_5)\text{I}$ (33). The average cobalt-carbon (cyanide) bond length of the four equatorial bonds is 1.894 Å while that of the axial bond is 1.927 Å; the cobalt-carbon (fluoroalkyl) bond length is only 1.990 Å. The difference in the σ -bond radius of carbon in its formal sp^3 and sp valence states is 0.06 to 0.07 Å so that the axial metal-cyanide and metal-fluoroalkyl bonds are equivalent. Since the cyanide ion is a moderate π -accepting ligand, the immediate inference is that the $\text{-CF}_2\text{CF}_2\text{H}$ ligand has comparable π -acceptor properties. The use of σ^* levels on the perfluoroalkyl groups for back-donation has been suggested by King (105), Cotton (41), Wilford and Stone (154), and Cotton and McCleverty (43). The latter authors show that the carbon-fluorine stretching modes of $\text{CF}_3\text{Mn}(\text{CO})_5$ occur some 100 cm^{-1} lower than those in simple perfluoromethyl compounds such as CF_3Cl . However, in spite of this data and the bond lengths, an unequivocal assessment of the relative contributions of σ - and π -bonding to the total bond order of the M-C bond is difficult. In the case of iodocarbonyl- π -cyclopentadienylpentafluoroethylrhodium (33), the difference between the Rh-C (carbonyl) and $\text{Rh-C}(\text{C}_2\text{F}_5)$ bond lengths is only 0.04 Å (after correction for the carbon σ -bond radius dependence on hybridization). Now the implication is that the $\text{-C}_2\text{F}_5$ group has comparable π -acceptor properties to the carbonyl group whereas in the first-row complex, the

suggestion was that the $-\text{CF}_2\text{CF}_2\text{H}$ group was similar to the cyanide ligand, which is certainly a weaker Lewis acid than the carbonyl ligand. The need for more structural data is obvious but one point might be borne in mind; the high-lying σ^* levels, which the metal d orbitals must use for back-donation, must overlap to a greater extent with $4d$ metal orbitals than will be the case for $3d$ orbitals.

The available data are summarized in Table V.

TABLE V
TRANSITION METAL-CARBON BOND LENGTHS

Complex	Bond	$d_{\text{M-C}}$ (Å)	Δ (Å) ^c
5,6-Dimethylbenzimidazolylcobamide coenzyme ^a	Co—CH ₂	2.05 ± 0.05	—
<i>trans</i> -Dimesitylbis(diethylphenylphosphine)cobalt ^b	Co—C(aryl)	1.96 ± 0.94	—
$\text{K}_3[\text{Co}(\text{CN})_5\text{CF}_2\text{CF}_2\text{H}]$	Co—CF ₂	1.990 ± 0.014	—
	Co—CN(<i>trans</i>)	1.927 ± 0.014	(-0.007 Å)
$\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{C}_2\text{H}_5$	Mo—CH ₂	2.40 ± 0.03	0.36
	Mo—CO	1.97 ± 0.03	—
$\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{C}_3\text{F}_7^d$	Mo—CF ₂	2.28 ± 0.02	0.22
	Mo—CO	1.99 ± 0.02	—
$\pi\text{-C}_5\text{H}_5\text{Rh}(\text{CO})\text{C}_2\text{F}_5\text{I}$	Rh—CF ₂	2.08 ± 0.03	0.04
	Rh—CO	1.97 ± 0.03	—
$(\text{OC})_2\text{Fe}(\pi\text{-C}_5\text{H}_4)\text{—CH}_2\text{Fe}^*(\text{CO})_4$	Fe*—CH ₂	2.123 ± 0.015	0.24
	Fe*—CO(<i>trans</i>)	1.809 ± 0.015	—
$\pi\text{-C}_5\text{H}_5\text{Re}(\text{CH}_3)_2\text{C}_5\text{H}_5\text{CH}_3$	Re—CH ₃ (av)	2.25 ± 0.03	0.18
	Re—CO	$< 2.00^e$	—
<i>cis</i> -(HCF ₂ CF ₂) ₂ Fe(CO) ₄ ^f	Fe—CF ₂ (av)	2.068 ± 0.014	0.15
	Fe—CO(av)	1.845 ± 0.014	—

^a From Lenhert and Hodgkin (107a).

^b From Owston and Rowe (121a).

^c Δ (Å) is the contraction of metal-carbonyl (or cyanide) group relative to the metal-alkyl (or fluoroalkyl) distance after correction has been made for the dependence of the σ -bond radius of carbon on hybridization.

^d From Churchill and Fennessey (24a).

^e Estimated for $\text{Re}_2(\text{CO})_{10}$ by comparison with bond lengths in $\text{Mn}_2(\text{CO})_{10}$ and $\text{Tc}_2(\text{CO})_{10}$ and recognizing that a Re^{V} -CO bond will be shorter than that found in the carbonyl.

^f From Churchill (34d).

The structural analysis of $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{C}_3\text{F}_7$ is particularly significant since it allows a direct comparison of the metal-carbon bond lengths in this

molecule with the molybdenum-ethyl complex; the stereochemistry of the molybdenum in these two complexes is essentially identical. In keeping with our earlier remarks, it will be of interest to compare bond lengths in isostructural alkyl and fluoroalkyl complexes of the first-row transition metal ions.

VII

METAL CARBONYLS AND SUBSTITUTED CARBONYLS

This subject is one on which a number of reviews have been written in the past and we have therefore felt the need to highlight only a very small section of the recent literature.

For the present reviewers, the single structural study most worthy of comment is that of the $[\text{HFe}_3(\text{CO})_{11}]^-$ ion since it appears to indicate, at

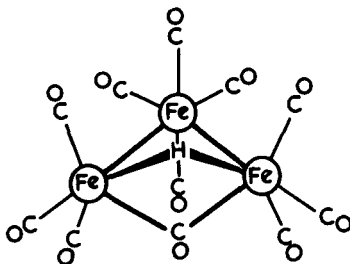


FIG. 37. The structure of the $[\text{HFe}_3(\text{CO})_{11}]^-$ ion, which gave the first indications of the true structure of $\text{Fe}_3(\text{CO})_{12}$.

last, the likely structure of $\text{Fe}_3(\text{CO})_{12}$ (53). The original X-ray study of $\text{Fe}_3(\text{CO})_{12}$ by Dahl and Rundle (46) suggested that the irons were located at corners of a triangle of sides 2.73, 2.75, and 2.64 Å in length although a complete structural analysis has not proved possible. By contrast, a number of Mossbauer resonance experiments suggested that the iron atoms lay in a straight line. The crystal structure analysis of $[(\text{C}_2\text{H}_5)_3\text{NH}][\text{HFe}_3(\text{CO})_{11}]$ shows that the iron atoms in the $[\text{HFe}_3(\text{CO})_{11}]^-$ ion are arranged as an isosceles triangle with two equivalent sides of 2.69 Å and one of 2.58 Å (Fig. 37). The anion has approximately C_s symmetry with one bridging carbonyl group and a (presumed) bridging hydrogen atom. The bridging hydrogen atom is replaced by a second bridging carbonyl to make up the proposed structure of $\text{Fe}_3(\text{CO})_{12}$ which has approximately C_{2v} symmetry and can alternatively be regarded as being formed by the substitution of an

$\text{Fe}(\text{CO})_4$ group at one of the bridging carbonyl positions in $\text{Fe}_2(\text{CO})_9$. Interestingly, the proposed structure of $\text{Fe}_3(\text{CO})_{12}$ is quite different from that of the isoelectronic $\text{Ru}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$ (35).¹

A field which will undoubtedly receive increasing attention in the future is that of polyborane metal carbonyl and carborane-metal carbonyl chemistry. The first polyborane-transition metal carbonyl complex to be

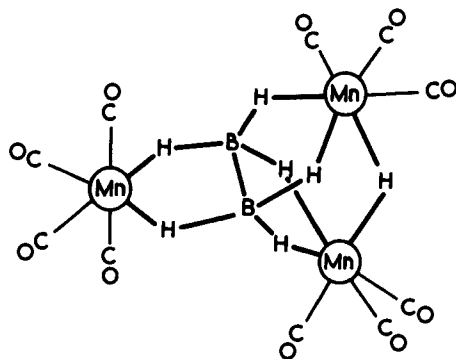


FIG. 38. The molecular structure of $\text{HMn}_3(\text{CO})_{10}(\text{BH}_3)_2$.

reported is $\text{HMn}_3(\text{CO})_{10}(\text{BH}_3)_2$ (96). The structure is represented in Fig. 38, which shows that the manganese atoms, separated by 2.85 Å, are bridged by BH_2 groups and that all three hydrogens of each BH_3 group are coordinated to other atoms via three-center bonds. A possible structure for the $((\text{B}_9\text{C}_2\text{H}_{11})\text{Mn}(\text{CO})_3)^-$ and $((\text{B}_9\text{C}_2\text{H}_{11})\text{Re}(\text{CO})_3)^-$ anions has been described (83) and details of an X-ray study are expected to show similarities with $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_3$ in the same way as the $(\text{B}_9\text{C}_2\text{H}_{11})^{2-}$ derivatives of iron (84) and cobalt (85) are related to ferrocene. The crystal structure of $\text{C}_5\text{H}_5\text{Fe}(\text{B}_9\text{C}_2\text{H}_{11})$ has a staggered sandwich structure (Fig. 39) (159).

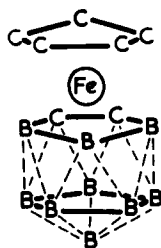


FIG. 39. The structure of $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{B}_9\text{C}_2\text{H}_{11})$, showing the staggered relationship of the cyclopentadienyl and the icosahedral cage.

¹Note added in proof: The proposed structure of $\text{Fe}_3(\text{CO})_{12}$ has now been directly confirmed [L. F. Dahl and C. H. Wei *J. Amer. Chem. Soc.* **88**, 1121 (1966)].

As the structural studies have increased both in accuracy and in number, the nature of metal-carbonyl bonds is being discussed in more detail than has hitherto been possible. The geometry of the equatorial carbonyls surrounding the manganese atoms in $\text{Mn}_2(\text{CO})_{10}$ has been discussed (18). The interesting fact has emerged that in $\text{Mn}_2(\text{CO})_{10}$ (49), $\text{Tc}_2(\text{CO})_{10}$ (7), $\text{Mn}(\text{CO})_5\text{H}$ (107), and $(\text{Et}_3\text{P})_2\text{Mn}_2(\text{CO})_8$ (19) the metal atoms do not lie exactly in the planes containing the equatorial carbonyl carbon atoms. In $\text{Mn}_2(\text{CO})_{10}$ and $\text{Tc}_2(\text{CO})_{10}$, for example, the two sets of carbonyl groups lean towards one another—a surprising result, in a sense, since it would seem to increase repulsions between these nonbonded groups. This distortion from an ideal geometry can, however, be shown (18) to lead to a decrease in the repulsions between nonbonding electron pairs on the metal ions.

A very general observation of the structures of metal carbonyls and metal cyanides is that the $\text{M}-\text{C}\equiv\text{O}$ and $\text{M}-\text{C}\equiv\text{N}$ bond angles show systematic deviations from a value of 180° . An explanation has recently been given (100) for the case of $\text{M}(\text{CO})_3$ fragments. Symmetry consideration shows that the π^* electron density of each complexed CO group will only possess twofold rotational symmetry and the $\text{M}-\text{C}-\text{O}$ bonds will be bent; this bending is a function of the difference in population of the two π^* orbitals. If the ligands *trans* to the tricarbonyl fragment do not possess a cylindrically symmetric bonding electron distribution, the population of the π^* acceptor levels on the carbonyl groups may vary one to another. A wide range of structures are now known which fall into this category; their geometries are summarized in Tables VI and VII (101). Correlations such as these will increase in value as higher precision of structural determination is obtained (as it inevitably will over the next 2 to 3 years).

TABLE VI
CARBONYL BOND ANGLES IN MOLECULES CONTAINING NEAR-CYLINDRICAL SYMMETRY

Molecule	(O)C—M—C(O) (degrees)	M—C—O (degrees)	References
$\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_3$	$91^\circ, 91^\circ, 94^\circ$	$178^\circ, 180^\circ, 176^\circ$	20
$\text{Fe}_3(\text{CO})_{15}\text{C}$ (unique iron atom)	$95^\circ, 96^\circ, 96^\circ$	$172^\circ, 168^\circ, 176^\circ$	23
$\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$	$89^\circ, 89^\circ, 86^\circ$	$180^\circ, 179^\circ, 179^\circ$	9
$\text{C}_6(\text{CH}_3)_6\text{Cr}(\text{CO})_3$	$90^\circ, 89^\circ, 89^\circ$	$177^\circ, 178^\circ, 177^\circ$	8

TABLE VII
CARBONYL BOND ANGLES IN MOLECULES SHOWING APPRECIABLE
DEVIATIONS FROM CYLINDRICAL SYMMETRY

Molecule	(O)C—M—C(O) (degrees)	M—C—O (degrees)	References
Co ₂ (CO) ₈	95°, 102°, 106°	175°, 176°, 177°	145
[C ₂ H ₅ SFe(CO) ₃] ₂	91°, 100°, 104° 86°, 99°, 101°	168°, 175°, 175° 178°, 169°, 169°	51
C ₆ F ₈ Fe(CO) ₃	90°, 101°, 101°	173°, 178°, 178°	27, 34
[(CF ₃) ₄ C ₅ O]Fe(CO) ₃	89°, 95°, 98°	179°, 176°, 176°	12, 13
(C ₆ H ₅ C ₂ H) ₃ Fe ₂ (CO) ₄	92°, 95°, 99°	176°, 176°, 178°	104
C ₈ H ₈ Fe ₂ (CO) ₈	91°, 101°, 102°	173°, 177°, 176°	56
C ₈ H ₈ Fe(CO) ₃	93°, 101°, 101°	173°, 178°, 178°	56
Fe ₅ (CO) ₁₅ C (equivalent iron atoms)	89°, 94°, 96° 99°, 95°, 91° 89°, 93°, 102° 92°, 93°, 96°	175°, 175°, 180° 170°, 174°, 175° 179°, 173°, 174° 169°, 172°, 177°	23
C ₄ H ₄ SCr(CO) ₃	91°, 91°, 88°	175°, 175°, 175°	10

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Structural Aspects of Organotin Compounds

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I. Introduction	137
A. Scope	137
B. Historical Aspects	138
II. Configurations	139
A. Survey of Configurations	139
B. Theoretical Considerations	144
C. A Criterion for the Configurations of the SnC_3 and SnC_2 Moieties	145
III. Representative Results	146
A. $(\text{CH}_3)_3\text{SnX}$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$)	146
B. $(\text{CH}_3)_2\text{SnX}_2$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$)	148
C. $\text{R}_3\text{SnOOCR}'$	148
D. $\text{R}_2\text{Sn}(\text{OOCR}')_2$	150
E. $\text{ClR}_2\text{SnOOCR}'$ ($\text{R}' = \text{CH}_3, \text{H}$)	151
F. $(\text{CH}_3)_3\text{SnOH}$	151
G. $(\text{CH}_3)_3\text{SnNO}_3$	153
H. $(\text{CH}_3)_3\text{SnX} \cdot \text{Pyridine}$ ($\text{X} = \text{Cl}, \text{NCS}$)	154
I. $[(\text{CH}_3)_3\text{SnD}_2]^+$ ($\text{D} = \text{NH}_3, \text{H}_2\text{O}$)	155
J. $\text{R}_2\text{SnX}_2 \cdot \text{D}_2$	155
K. $[(\text{CH}_3)_3\text{SnX}_2]^-$, $[(\text{CH}_3)_2\text{SnX}_4]^{2-}$, and $[\text{CH}_3\text{SnX}_5]^{2-}$ ($\text{X} = \text{halogen}$ or NCS)	155
L. $\text{R}_3\text{Sn}(\text{ox})$	156
M. $\text{R}_2\text{Sn}(\text{ox})_2$	157
N. $\text{XR}_2\text{Sn}(\text{ox})$	158
O. $\text{R}_2\text{Sn}(\text{acac})_2$	158
P. $\text{RSn}(\text{OOCR}')_3$ and $\text{C}_6\text{H}_5\text{Sn}(\text{tropolonato})_3$	158
IV. Organostannoxanes	159
A. Introduction	159
B. The Dimeric Structure and Properties of $\text{XR}_2\text{SnOSnR}_2\text{X}$ and $\text{XR}_2\text{SnOSnR}_2\text{OH}$	161
C. Polymeric Organotin Oxides	164
References	165

I

INTRODUCTION

A. Scope

This article reviews the structures of those organotin compounds which possess a tin atom having an essential valency of four but having coordination

greater than four. The chemistry of such compounds has developed quite recently and is still actively being studied. Knowledge of the structure and reactions of these substances may serve as a basis for investigation of the kinetics of organotin reactions.

Numerous investigations of tetraalkyldistannoxane derivatives have been reported since the nineteenth century. However, only recently has the unique structure and chemistry of these compounds been understood. A separate section is devoted to the description of this latter work.

B. Historical Aspects

Advances in the structural chemistry of organotin compounds occupy a prominent position among recent developments in the field of organo-metallic chemistry. The chemistry of organotin compounds through the end of 1959 has been exhaustively reviewed by Ingham *et al.* (1). However, very little structural information appears in this review, because the first systematic structural studies were initiated only after it appeared.

Interest arose at this time in the marked chemical and physical differences between organosilicon and organotin compounds. Differences between the infrared spectra of methylacetoxysilanes and methyltin carboxylates were interpreted in 1960 by Okawara *et al.* (2) in terms of ester-type bonding for the silicon acetates and ionic structures for the tin compounds. Similar observations on methyltin group absorptions in the spectra of trimethyltin halides also suggested an ionic structure for $(\text{CH}_3)_3\text{SnF}$ with a planar trimethyltin cation. These interpretations were questioned by Beattie and Gilson (3), and later investigations have shown that these compounds have polymeric structures with bridging by anionic species.

Another structural aspect of organotin chemistry is associated with the elucidation of the marked differences in chemical and physical properties of the polymeric diorganotin oxides in contrast to the corresponding diorganopolysiloxanes. Diorganotin oxides are usually insoluble, amorphous, and infusible materials, whereas polymeric diorganopolysiloxanes are viscous liquids, soluble in many organic solvents. Okawara (4) suggested, from molecular weight determinations and an X-ray analysis, that tetraalkyl 1,3-disubstituted distannoxanes, $\text{XR}_2\text{SnOSnR}_2\text{X}$ [$\text{X}=\text{OSi}(\text{CH}_3)_3$, $\text{R}=\text{CH}_3$; $\text{X}=\text{Cl}$, $\text{R}=\text{C}_2\text{H}_5$, $n\text{-C}_3\text{H}_7$, $n\text{-C}_4\text{H}_9$], have a dimeric structure. The establishment of this structure advanced understanding of the chemistry of the

polymeric diorganotin oxides and of the partial hydrolysis products of a wide variety of diorganotin derivatives.

A third interest in structural problems originated from the study of the organotin addition compounds. Organotin halides, like the tetrahalides of tin, react with electron-pair donors to form addition compounds of the type $R_xSnX_{4-x} \cdot nD$ (where X = halogen, and D = an electron-pair donor). Earlier workers (5) favored an ionic formulation for compounds such as $(CH_3)_3SnCl \cdot \text{pyridine}$, which were represented as analogous to quaternary nitrogen $[(CH_3)_3Sn \cdot \text{pyridine}]^+Cl^-$. Further, the compound $(CH_3)_2SnCl_2 \cdot 2(\text{pyridine})$ is apparently a weak electrolyte in acetonitrile (6). In 1963, Beattie and McQuillan (7) observed the infrared spectra of these compounds and deduced that they contain pentacoordinate or hexacoordinate tin, by analogy with the spectra of addition compounds of inorganic tin halides which contain tin with a coordination number larger than four. An X-ray diffraction study (8) confirms this interpretation.

A fourth interest originated from the preparative works of Blake *et al.* (9) of some organotin derivatives containing chelating ligands, such as 8-hydroxyquinoline.

All of the above investigations have shown that the coordination number of the tin atom in organotin derivatives can be greater than four. A recent review by Beattie (10) deals with the acceptor properties of the fourth main group elements, and a short review on the coordination chemistry of organotin compounds has been published by Poller (11). The rapid and continuing development in this area has necessitated a more detailed survey.

II

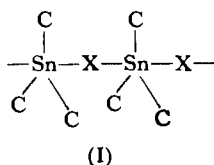
CONFIGURATIONS

A. Survey of Configurations

In organotin derivatives, tetrahedral configuration around the tin atom is generally observed. Even in the compounds represented by the formula $(R_2Sn)_x$, all the tin valence orbitals are usually employed leading to tin-tin bonds and to tetravalent tin (12). However, if one or more of the alkyl groups in a tetraorganotin molecule, R_4Sn , are replaced by anionic atoms or groups, the tin atom in the resulting compounds often exhibits a coordination number greater than four. Pentacoordinated tin atoms are found in

triorganotin derivatives, but no triorganotin compounds containing hexa-coordinated tin have been observed.

The most general feature of pentacoordinated tin is a polymeric structure formed by the bridging of an anionic group to the tin atom from either side of the plane of the trialkyltin group. This kind of structure is designated as type (I).



Type (I) compounds can be divided into three subgroups, as shown in Table I.

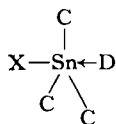
TABLE I
GROUPING OF COMPOUNDS OF STRUCTURE TYPE I

Subgroup	Compound
(a)	(CH ₃) ₃ SnF (Section III, A), (CH ₃) ₃ SnOH (Section III, F)
(b)	R ₃ SnOOCR' (Section III, C), (C ₄ H ₉) ₃ Sn(imidazole) (13, 14), (CH ₃) ₃ SnNO ₃ (Section III, G), (CH ₃) ₃ SnClO ₄ (15, 16), (CH ₃) ₃ SnBF ₄ (17, 18), (CH ₃) ₃ SnAsF ₆ (18), (CH ₃) ₃ SnSbF ₆ (18), R ₃ SnAlCl ₄ (19)
(c)	(CH ₃) ₃ SnCl (Section III, A), (CH ₃) ₃ SnBr (Section III, A), (CH ₃) ₃ SnCN (20), R ₃ SnNNN (21, 22), (CH ₃) ₃ SnNCS (23, 24), (CH ₃) ₃ SnNCO (23)

The compounds in the (a) subgroup of this classification contain tin atoms bridged by a single atom. The tin atoms of the (b) subgroup compounds are bridged by the anionic groups in the manner, —Sn—X—Z—X—, where X represents a halogen, an oxygen, or a nitrogen atom and Z represents the remainder of the resulting group. The compounds in both (a) and (b) subgroups are assumed to contain planar SnC₃ moieties, but in so far as they have been studied, those compounds in the (c) subgroup have no such planar moiety.

In compounds of structure type (II), a donor molecule is coordinated to a triorganotin halide to give a trigonal bipyramidal arrangement. The best

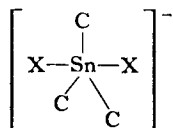
studied example is the 1:1 addition compound of $(\text{CH}_3)_3\text{SnCl}$ and pyridine mentioned above, whose structure is fully described in Section III, H.



(II)

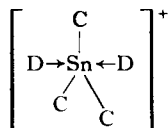
D = donor molecule

A halide ion can also act as a Lewis base to trimethyltin halide, giving a symmetrical bipyramidal configuration, of type (III)



(III)

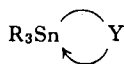
In cases where the anionic groups have no coordinating sites, for example, $[\text{B}(\text{C}_6\text{H}_5)_4]^{-}$ (Section III, I), two molecules of a nonanionic Lewis base such as water can occupy the coordination sphere, giving a planar SnC_3 arrangement with a pentacoordinated tin atom. This is shown below as type (IV).



(IV)

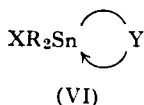
This finding may well be applied to interpret the structure of 1:2 addition compounds of formula $\text{R}_3\text{SnX} \cdot 2\text{D}$ (I) as that containing a bipyramidal $[\text{R}_3\text{SnD}_2]^{+}$ and X^{-} anion, and may preclude the existence of hexacoordinated tin atoms in such triorganotin complexes.

If the X group in R_3SnX belongs to a chelating ligand, intramolecular coordination can occur as shown in structure (V). The triorganotin oxinates provide examples of this type of structure (Sections III, L).

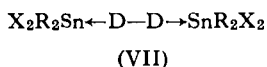


(V)

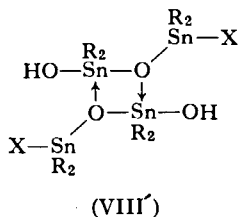
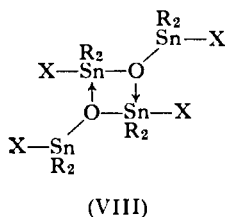
In the case of diorganotin derivatives, both pentacoordinated and hexacoordinated tin compounds have been reported. Pentacoordinated tin is observed in dialkyltin halide carboxylates, dialkyltin halide oxinates (Section III, N), and dimethyl(1,3-dimethyltriazeno)tin halides (25). This structure type is represented in Formula (VI). In this case the chelating ligand may be either symmetrical or unsymmetrical.



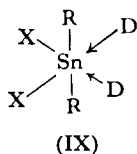
The 2:1 addition compound of $(\text{C}_6\text{H}_5)_2\text{Sn}(\text{NCO})_2$ and bipyridine is another type of pentacoordinated diorganotin structure (VII) (26).



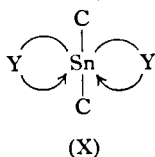
The dimeric tetraalkyldistannoxanes, $[\text{XR}_2\text{SnOSnR}_2\text{X}]_2$ and $[\text{XR}_2\text{SnOSnR}_2\text{OH}]_2$, are unique, because the molecule contains both tetracoordinated and pentacoordinated tin atoms (Section IV). The structures are shown in (VIII) and (VIII').



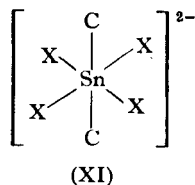
Infrared spectroscopic investigations have shown that the addition compounds of R_2SnX_2 (X = halogen) and monodentate amines in 1:2 mole ratio, or bidentate amines in 1:1 mole ratio, are structures of type (IX) (7).



Many diorganotin bis(chelates) have been isolated (9, 25, 27–35) and found to contain hexacoordinated tin atoms. Some representative compounds are acetylacetonates, oxinates, and carboxylates (Sections III, D, M, and O). It has been found that the alkyl groups in these compounds exist predominantly in the *trans* positions, as shown in type (X). Again, symmetrical and nonsymmetrical chelating ligands may form these structures.

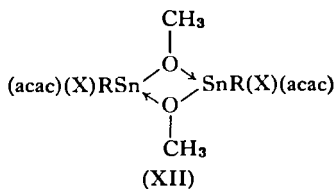


The most symmetric species is the $[(\text{CH}_3)_2\text{SnX}_4]^{2-}$ anion ($\text{X} = \text{F}, \text{Cl}, \text{NCS}$), whose structure is represented by (XI) (Section III, K). Tobias *et al.* have shown that there are analogous species, $[(\text{CH}_3)_2\text{Sn}(\text{OH})_4]^{2-}$, as well as cationic hydrated species, in aqueous solution of dimethyltin compounds (32, 36, 37).



Reports on monoorganotin compounds indicate that some of them might have hexacoordinated and even heptacoordinated tin atoms. However, little work has been done on their detailed configurations. Monoorganotin halide bis acetylacetonates (38) and bis oxinates (39, 40), as well as the addition compounds of formula $\text{RSnX}_3 \cdot 2\text{D}$ (7), are examples of hexacoordinated tin compounds.

The complex compound, $[(\text{acac})\text{XRSn}(\text{OCH}_3)]_2$, obtained by the partial alcoholysis from $\text{RXSn}(\text{acac})_2$ is unique in that it contains two bridging methoxy groups forming a four-membered Sn—O ring (41), as shown in structure (XII).



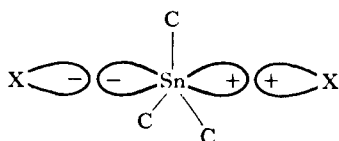
A heptacoordinated tin is observed in phenyltin tris(tropolonate), and probably in monoorganotin tris(carboxylates) (Section III, P).

B. Theoretical Considerations

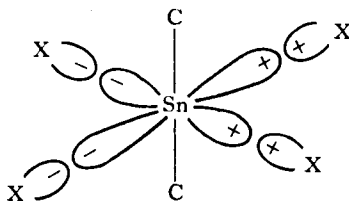
In an organotin compound the tin atom can assume a coordination number greater than four if one or more of the four Sn—R bonds are replaced by anionic atoms or groups. The extra bonding which can not be explained by the essential valency of tin(IV) may be understood as originating from the positive charge on the tin atom, which is necessary in order to maintain an overall charge close to zero.

According to the familiar valence-bond theory of directed orbitals, the bonding in penta-, hexa-, or heptacoordinated structures is described in terms of the hybridization of the $5s$, $5p$, and $5d$ orbitals of tin. However, the so-called "three-center molecular orbitals" based on $p\sigma$ atomic orbitals have been cited to interpret the coordination bonding (7, 30), because in the tin atom there may be appreciable separation in the p — d energies and because the d orbitals may be rather diffuse in compounds which do not possess a number of highly electronegative substituents.

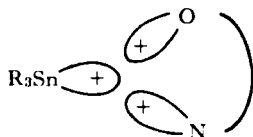
In bipyramidal structures such as (I) to (IV) in the previous section, the three Sn—C bonds are represented with essentially sp^2 hybridization. The remaining p orbital can participate in linear three-center bonds in the manner shown below, where X represents the coordinating atoms or ions.



In octahedral structures such as (IX), (X), or (XI), the two bonds in the linear C—Sn—C moiety may be constructed essentially with sp hybridization of the tin atom. The remaining two p orbitals of tin can form two sets of three-center bonds in the plane perpendicular to the C—Sn—C axis, as shown below.



If some of the Sn—X bonds become more covalent both in the triorganotin and in the diorganotin complex compounds, the tin 5s character should become more uniformly distributed among those bonds including the Sn—C covalent bonds. Examples of this have been observed by proton magnetic resonance spectroscopy for several *trans* octahedral complexes of the dimethyltin cation (30). When the bonds in the type (V) structure of triphenyltin oxinate are represented with three-center molecular orbitals based on the $p\sigma$ atomic orbital of tin, the Sn—R bond opposite to the Sn—N coordination bond must participate in the three-center bond. However, this result is not in accord with the assumed high covalency of the Sn—R bond. However, delocalized bonding can be used to explain these compounds if a hybridized sp^3 orbital of tin is used. This orbital could participate in bent three-center bonds with the appropriate orbitals of oxygen and nitrogen.



In some other types of structures, the configurations around the tin atom are not definitely known. However, the theory of valency shell electron-pair repulsions, which is essentially based on the valence-bond theory, usually provides good predictions for the configuration of polycoordinated compounds (42–44). According to this theory, the preferred arrangement of five valence electron pairs is the trigonal bipyramid, in which the bonding electron pairs attaching a ligand of lesser electronegativity tend to occupy the equatorial positions. Thus, in the pentacoordinated structures of diorganotin derivatives, the two Sn—C bonds would tend to occupy the equatorial positions of the bipyramidal configuration, resulting in an essentially nonlinear arrangement of the C—Sn—C moiety.

C. A Criterion for the Configurations of the SnC_3 and SnC_2 Moieties

Infrared spectroscopy has provided valuable information on the configuration of organotin compounds. Particularly important is the criterion established for determining the configuration of SnC_3 and SnC_2 moieties in trimethyltin and dimethyltin derivatives. If the spectrum reveals two

Sn—C stretching vibrations (both the symmetric and the asymmetric modes), the configuration of SnC_3 group is nonplanar or that of SnC_2 is nonlinear. However, if there is only one band assignable to an Sn—C stretching vibration, the configuration of SnC_3 group is planar or that of SnC_2 is linear (2). Many researchers have applied this simple criterion to deduce the configuration around a tin atom. In some cases the appropriateness of this criterion has been supported by X-ray analysis.

III

REPRESENTATIVE RESULTS

A. $(\text{CH}_3)_3\text{SnX}$ ($\text{X}=\text{F}, \text{Cl}, \text{Br}, \text{I}$)

Among the trimethyltin halides, $(\text{CH}_3)_3\text{SnF}$ is markedly different in physical and chemical properties from the remaining halides; the fluoride has no definite melting point, and decomposes at 375° , while the other halides melt below 35° and can be distilled at low temperatures. The crystals of the fluoride consist of bundles of very fine colorless needles.

The infrared spectrum of $(\text{CH}_3)_3\text{SnF}$ was investigated by Okawara *et al.* (2); it shows only one strong absorption in the Sn—C stretching region at 555 cm^{-1} . This indicates a planar arrangement of the SnC_3 moiety. For the other halides, two absorptions assigned to the symmetric and asymmetric Sn—C stretching vibrations are observed, in accord with a tetrahedral configuration about the tin atom. These results were interpreted in terms of an ionic structure for the fluoride and a covalent structure for the other halides (2).

Later, an X-ray study of $(\text{CH}_3)_3\text{SnF}$ was reported by Clark *et al.* (45), who showed that the structure of this compound is composed of trimethyltin groups and fluorine atoms arranged alternately along the needle axis. However, the determination of the positions of the light atoms was not definitely settled. Two interpretations of the three-dimensional electron density distribution were proposed. In both models, essentially penta-coordinated tin atoms and nonlinear Sn—F—Sn bridges were assumed. One proposed structure has nonplanar trimethyltin groups, which are ordered in a chain, while the fluorine atoms are disordered, occupying any position on parts of a spherical surface about 2.1 \AA from a tin atom. In the second structure, the SnC_3 skeletons are planar and tilted alternately with respect to the axis of needle crystal (45).

The electron density distribution has been elucidated with the aid of far-infrared and Raman spectroscopy (46). The far-infrared spectrum showed a broad strong band at 350 cm^{-1} . In the Raman spectrum a weak band at

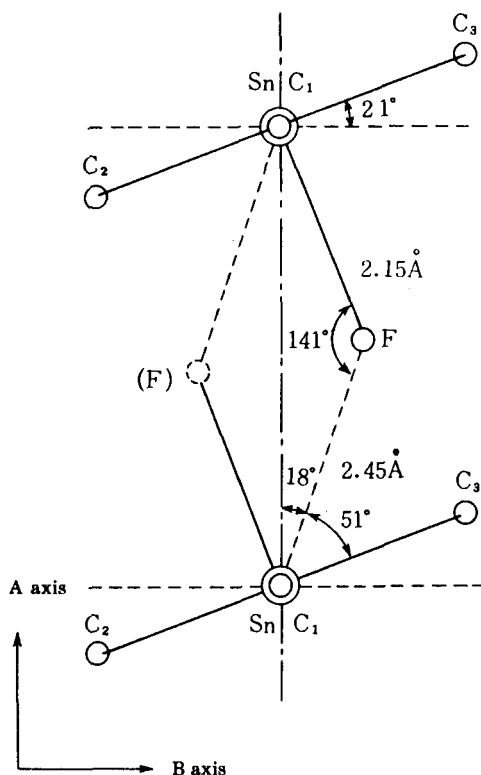


FIG. 1. A projection of the probable crystal structure of trimethyltin fluoride down to the (001) plane. F and (F) indicate the two possible positions of fluorine atoms of the same potential energy.

556 cm^{-1} and a strong band at 517 cm^{-1} were observed, but no band assignable to Sn—F symmetric stretching was found in the region down to 150 cm^{-1} . The Sn—F symmetric stretch must be Raman-active, so it can be deduced that the band at 350 cm^{-1} in the far-infrared spectrum is due to the asymmetric Sn—F stretching. The absence of a Raman-active Sn—F symmetric stretching vibration in the recorded region was interpreted as follows: the planar trimethyltin group is bridged by the fluorine atom forming a nonlinear unsymmetrical Sn—F—Sn bond. Using this latter

observation, and the results of the X-ray diffraction study, the structure shown in Fig. 1 has been arrived at. The planes of the trimethyltin group are parallel but incline about 21° from the plane perpendicular to the needle axis. The fluorine atoms still take the positions in the space between these planes but with different bond lengths to the adjacent tin atoms.

The far-infrared and Raman spectra of $(\text{CH}_3)_3\text{SnCl}$ and $(\text{CH}_3)_3\text{SnBr}$ in various states give Sn—X stretching vibration bands at different frequencies in each state (47). For example, the Sn—Cl stretching vibration band occurs at 288 cm^{-1} in the solid, at 315 cm^{-1} in the liquid, and at 331 cm^{-1} in CS_2 solution. These observations suggest the occurrence of Sn—X—Sn association in the solid and even in the liquid state. However, the marked differences between the physical properties of these halides and those of $(\text{CH}_3)_3\text{SnF}$ imply a fundamental difference between the manner of association of $(\text{CH}_3)_3\text{SnF}$ and that of the other halides. The results of an electron diffraction study of gaseous $(\text{CH}_3)_3\text{SnCl}$, $(\text{CH}_3)_3\text{SnBr}$, and $(\text{CH}_3)_3\text{SnI}$ (48), confirm the tetrahedral configuration for these molecules.

B. $(\text{CH}_3)_2\text{SnX}_2$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$)

In the infrared spectra of these dihalides, a band characteristic of dimethyltin compounds and assigned to symmetric Sn—C stretching vibration is shown at 515 cm^{-1} by the chloride, at 514 cm^{-1} by the bromide, and at 511 cm^{-1} by the iodide (2), but the fluoride does not give a corresponding band (49). This compound has a band due to the asymmetric Sn—C stretching vibration at 598 cm^{-1} , but gives no appropriate band assignable to Sn—F stretching vibration in the $620\text{--}540\text{ cm}^{-1}$ region. By analogy with the result for $(\text{CH}_3)_3\text{SnF}$ described above, these observations support a polymeric structure for $(\text{CH}_3)_2\text{SnF}_2$. The SnC_2 moieties have linear arrangements and are bridged by fluorine atoms, resulting in a hexacoordinated tin atom.

C. $\text{R}_3\text{SnOOCR}'$

In 1960 Okawara *et al.* investigated the infrared spectra of some methyltin acetates and formates (2). They interpreted the spectra of trimethyltin carboxylates, e.g., $(\text{CH}_3)_3\text{SnOOCR}'$ ($\text{R}' = \text{H}$ and CH_3), in terms of ionic structures, since the spectra showed the existence of a planar trimethyltin group and indicated an ionic-type carboxylate group. However, Beattie and

Gilson pointed out that the spectroscopic evidence might be interpreted in terms of either bridging carboxylate groups, or simple acetate ions (3). From viscosity measurements, Janssen *et al.* supported the bridging structure (50). More refined infrared (50, 51) and molecular weight studies (51) indicate that, in general, compounds of the formula $R_3SnOOCR'$ exist as linear polymers in the solid, and even in concentrated solutions of nonpolar solvents, but are monomeric in dilute solutions.

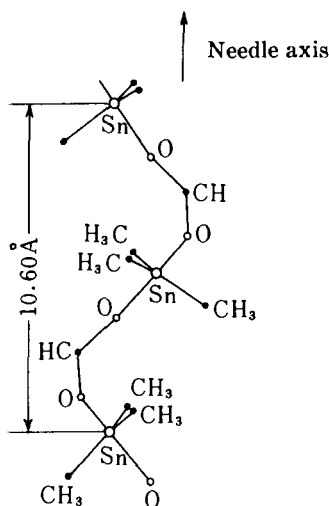


FIG. 2. A molecular chain of trimethyltin formate.

Some representative results are given here. Okawara and Ohara studied $(C_2H_5)_3SnOOCH$ and $(n-C_3H_7)_3SnOOCH$ by molecular weight determinations, infrared spectroscopy, and far-infrared spectroscopy (51). The molecular weights of these compounds increase linearly with increasing concentration, indicating the existence of low polymers in solution. In the infrared spectra of these compounds in the solid state, the formoxy group shows bands similar to those of the formate anion at near 1590, 1360, and 770 cm^{-1} ; furthermore a band which is due to a weak coordination of the oxygen atom with the tin atom is found near 300 cm^{-1} . The absorption due to the Sn—C stretching vibration appears only at 520 cm^{-1} in triethyltin formate. In the spectra of solutions, additional bands due to the terminal formoxy group appear near 1660, 1245, and 430 cm^{-1} . These facts indicate that in the solid state trialkyltin formate is a linear polymer in which the

planar SnC_3 moieties are bridged by the $-\text{OCO}-$ unit, and that even in solution this structure is partially maintained.

The X-ray diffraction of trimethyltin formate has recently been studied (52). The dimensions of the unit cell of this needle crystal are as follows: $a = 12.40 \text{ \AA}$; $b = 10.60 \text{ \AA}$; $c = 20.68 \text{ \AA}$; $\beta = 146.5^\circ$; $z = 8$; the space group, $P2_1/a$. This result indicates that the structure consists of a planar trimethyltin and a formoxy group arranged alternately along a helix chain. The tin atoms are pentacoordinated by three carbon atoms and two oxygen atoms. The plane of trimethyltin group is inclined from the crystal axis as shown in Fig. 2.

The identity periods (b) of needle crystals of the other trialkyltin carboxylates are shown in Table II. From Table II, it is seen that the identity periods fall in the range of $10.86\text{--}9.95 \text{ \AA}$, and it is expected from this observation that these carboxylates have analogous polymeric structures along the needle axis.

TABLE II
IDENTITY PERIODS OF $\text{R}_3\text{SnOOCR}'$

	M.p. ($^\circ\text{C}$)	I.P. (\AA)		M.p. ($^\circ\text{C}$)	I.P. (\AA)
$(\text{CH}_3)_3\text{SnOOCH}$	151°	10.60	$(n\text{-C}_3\text{H}_7)_3\text{SnOOCCH}_3$	$99\text{--}100^\circ$	10.36
$(\text{C}_2\text{H}_5)_3\text{SnOOCH}$	$57\text{--}58^\circ$	10.86	$(n\text{-C}_3\text{H}_7)_3\text{SnOOCCHCl}_2$	—	10.47
$(\text{CH}_3)_3\text{SnOOCCH}_3$	197°	10.55	$(n\text{-C}_4\text{H}_9)_3\text{SnOOCCH}_3$	$86\text{--}87^\circ$	10.46
$(\text{CH}_3)_3\text{SnOOCCH}_2\text{Cl}$	148°	10.10	$(n\text{-C}_4\text{H}_9)_3\text{SnOOCCH}_2\text{Cl}$	$56\text{--}56.5^\circ$	10.48
$(\text{CH}_3)_3\text{SnOOCCHCl}_2$	135°	9.95	$(n\text{-C}_4\text{H}_9)_3\text{SnOOCCH}_2\text{Cl}$	$59\text{--}60^\circ$	10.50
$(\text{C}_2\text{H}_5)_3\text{SnOOCCH}_3$	$134\text{--}135^\circ$	10.35	$(n\text{-C}_4\text{H}_9)_3\text{SnOOCCL}_3$	$78\text{--}80^\circ$	10.52

D. $\text{R}_2\text{Sn}(\text{OOCR}')_2$

The infrared spectrum of $(\text{CH}_3)_2\text{Sn}(\text{OOCH})_2$ shows bands associated with the COO group at 1588 cm^{-1} (antisym. str.) and 1390 cm^{-1} (sym. str.). The frequencies are quite similar to those observed for NaOOCH (2). Further, the spectrum reveals only one band in the KBr region, indicating a linear arrangement of SnC_2 moiety. The spectra of $(n\text{-C}_3\text{H}_7)_2\text{Sn}(\text{OOCCH}_3)_2$ and $(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{OOCCH}_3)_2$ show bands due to the COO stretching vibration at 1610 cm^{-1} and 1380 cm^{-1} (34). These bands are observed at the same

frequencies even in cyclohexane solution, in which the diacetates exist as monomers. These observations suggest a *trans* bis(chelate) configuration for this type of compound.

E. $\text{ClR}_2\text{SnOOCR}'$ ($\text{R}' = \text{CH}_3, \text{H}$)

The infrared spectrum of $\text{ClR}_2\text{SnOOCCH}_3$ in the solid state shows one of the characteristic bands associated with the antisymmetric stretching vibration of the COO group at $1540\text{--}1565\text{ cm}^{-1}$. In carbon tetrachloride or benzene solution the band shifts to near 1600 cm^{-1} . This indicates that some structural changes have occurred on solution, but still suggests a nonester type of acetoxy group. Molecular weight determinations show that these compounds are monomeric in benzene. With these observations a chelate structure has been proposed for the compounds in solution (53).

The infrared spectrum of $\text{ClR}_2\text{SnOOCH} \cdot \text{H}_2\text{O}$ in the solid state indicates the existence of formoxy groups of the ionic type, and it may be assumed that a hexacoordinated tin atom is involved in these monohydrates.

F. $(\text{CH}_3)_3\text{SnOH}$

$(\text{CH}_3)_3\text{SnOH}$ is unique in that it has a marked stability against condensation by dehydration, whereas other trialkyltin hydroxides are readily dehydrated to give hexaalkyldistannoxanes, $\text{R}_3\text{SnOSnR}_3$. The structure of the compound has been studied by means of nuclear magnetic resonance spectra (54), infrared spectra (55, 56), Raman spectra (55), far-infrared spectra (56), molecular weight measurement (56), and by X-ray diffraction (57).

The infrared spectra show that $(\text{CH}_3)_3\text{SnOH}$ has no hydrogen bridge either in the solid or in the solution states, although marked differences are observed between the spectra in these two states (Fig. 3). Ebulliometric molecular weight determinations of the compound in nonpolar solvents indicate a dimeric molecule $[(\text{CH}_3)_3\text{SnOH}]_2$. The three bands observed in the solution spectra in the range $580\text{--}500\text{ cm}^{-1}$ were assigned as due to the two Sn—C stretching vibrations (symmetric and asymmetric), and an Sn—O stretching vibration. In the solid spectra, the last vibration band is observed in far-infrared region, and only one Sn—C stretching vibration

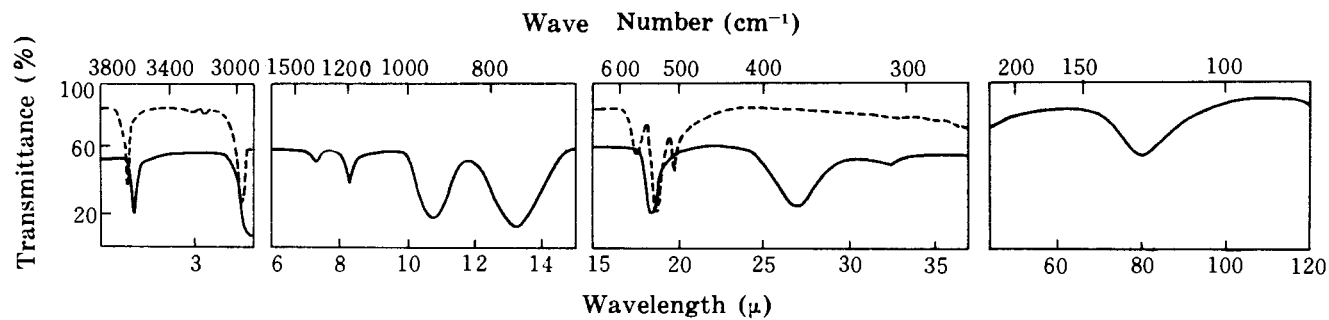
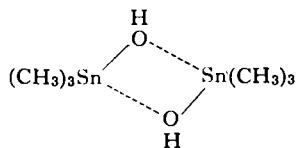
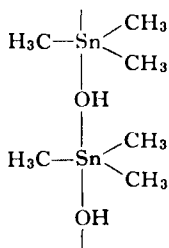


Fig. 3. Infrared absorption spectra of $(\text{CH}_3)_3\text{SnOH}$: —, Nujol or hexachlorobutadiene mull; ----, CCl_4 solution.

band is observed at 540 cm^{-1} . These observations were interpreted as indicating that the solid $(\text{CH}_3)_3\text{SnOH}$ is a linear polymer, in which the planar $(\text{CH}_3)_3\text{Sn}$ groups are weakly bridged by the $-\text{O}(\text{H})-$ units, whereas in solution it has a dimeric structure with a four-membered ring formed by the two oxygen bridges between two tin atoms.



Crystals of trimethyltin hydroxide, $(\text{CH}_3)_3\text{SnOH}$, are monoclinic. The dimensions of the orthorhombic subcell are as follows: $a' = 6.67$, $b' = 4.15$, $c' = 11.21\text{ \AA}$; $Z = 2$; the space group is $P2_1nm$. The structure, studied by X-ray diffraction, consists of chains of trimethyltin groups and hydroxyl groups arranged alternately along the b' axis, with the chains held together by weak van der Waals' forces between the methyl groups in neighboring chains. The oxygen atom lies on the axis of, and is almost equidistant between, two tin atoms. The trimethyltin group is nearly planar, which is consistent with the observed infrared spectrum, and inclined at about 15° with respect to the plane perpendicular to the chain axis. The X-ray reflections suggest some small disorders in the crystals and the extension to the true cell ($a = 2a'$, $b = 8b'$, $c = 2c'$) has also been studied (57).



G. $(\text{CH}_3)_3\text{SnNO}_3$

This compound was first suggested from study of its infrared spectrum to have a tetrahedral configuration around the tin atom (15, 16). The spectrum has been reinvestigated by Yasuda *et al.* (58) and Clark *et al.* (59). Yasuda *et al.* proposed the compound of melting point 140°C as the nitrate.

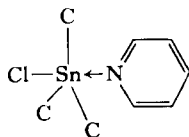
On the other hand, that with a melting point of 127°–128°C has been proposed by Clark *et al.* The spectra of an analytically purer compound (m.p. 140°C) showed that it contains a planar SnC_3 moiety and a lower symmetry of NO_3 groups, indicating the occurrence of the usual polymeric structure of triorganotin salts.

While there seems no reason to doubt the existence of monohydrate of $(\text{CH}_3)_3\text{SnNO}_3$ (58, 59), it seems that more confirmatory evidence is desirable in order to deduce the possible structure.

H. $(\text{CH}_3)_3\text{SnX} \cdot \text{Pyridine}$ ($X = \text{Cl}, \text{NCS}$)

Beattie and McQuillan (7) studied the infrared spectra of the 1:1 addition compound of $(\text{CH}_3)_3\text{SnCl}$ with pyridine. Only one band at 560 cm^{-1} was observed in the $\text{Sn}-\text{C}$ stretching region, and so planar arrangement of the SnC_3 moiety was indicated. The $\text{Sn}-\text{Cl}$ stretching vibration, which in trimethyltin chloride is observed around 330 cm^{-1} , is shifted to below 250 cm^{-1} . Beattie and McQuillan suggested a bipyramidal structure for the addition compound, and this was confirmed by X-ray diffraction (8). The molecule contains a pentacoordinated tin atom, the stereochemistry approximating a trigonal bipyramid with three methyl groups in the equatorial plane and an almost linear $\text{Cl}-\text{Sn}-\text{N}$ arrangement perpendicular to it. The $\text{Sn}-\text{Cl}$ distance is about 2.42 \AA , and no distance between nonbonded atoms is less than 3.5 \AA . The $\text{Sn}-\text{Cl}$ distance lies within the range of published values (60) for octahedral $\text{Sn}-\text{Cl}$ (2.39 – 2.45 \AA) but is 0.05 \AA greater than the tetrahedral $\text{Sn}-\text{Cl}$ distance of 2.37 \AA in $(\text{CH}_3)_3\text{SnCl}$ (48).

The infrared spectrum of the 1:1 pyridine complex of $(\text{CH}_3)_3\text{SnNCS}$ shows only one band due to the NCS bending vibration, though two bending modes were observed in the spectrum of $(\text{CH}_3)_3\text{SnNCS}$ itself (24). This observation was interpreted in terms of the linearity of the $\text{Sn}-\text{N}-\text{C}-\text{S}$ linkage. $(\text{CH}_3)_3\text{SnNCS}$, on the other hand, is assumed to have a bent $\text{Sn}-\text{N}-\text{C}$ linkage, which indicates a greater degree of covalent character in the $\text{Sn}-\text{N}$ bond.



I. $[(CH_3)_3SnD_2]^+$ ($D = NH_3, H_2O$)

Clark and O'Brien found that both $(CH_3)_3SnClO_4$ and $(CH_3)_3SnNO_3$ form diammonia adducts (16, 59). On the basis of their infrared spectra, the ionic structure, $[(CH_3)_3Sn(NH_3)_2]^+X^-$ ($X = ClO_4, NO_3$), in which the tin atom has a trigonal bipyramidal configuration, was proposed. That is, the observed frequencies in the infrared spectra of each complex were interpreted as those associated with a free ClO_4^- or a free NO_3^- ion, an essentially planar $(CH_3)_3Sn$ group, and coordinated NH_3 groups.

Wada and Okawara isolated a compound of composition $(CH_3)_3Sn \cdot B(C_6H_5)_4 \cdot 2H_2O$, by the reaction of $(CH_3)_3SnCl$ and $NaB(C_6H_5)_4$ in water (61). The infrared spectrum shows only one band at 562 cm^{-1} in the $580\text{--}500\text{ cm}^{-1}$ region, indicating a planar SnC_3 arrangement. The existence of bipyramidal $[(CH_3)_3Sn(OH_2)_2]^+$ ion in this compound is suggested.

J. $R_2SnX_2 \cdot D_2$

As in the case of the tin tetrahalides, 1:2 addition compounds of dialkyltin dihalide, R_2SnX_2 , with monodentate Lewis bases, and 1:1 addition compounds with bidentate Lewis bases exist (7, 28). In solution these compounds dissociate to a considerable extent. The absence of a symmetric $Sn\text{--}C$ stretching vibration in the infrared spectrum of solid $(CH_3)_2SnCl_2 \cdot 2(\text{pyridine})$ and $(CH_3)_2SnCl_2 \cdot \text{bipyridine}$ in the region $580\text{--}500\text{ cm}^{-1}$ suggests a coordination number of six for the tin atom with a *trans* alignment of the methyl groups (7, 28). The other striking aspect of the spectra is the absence of a band in the tin-chlorine stretching region ($330\text{--}300\text{ cm}^{-1}$).

The infrared spectra of $R_2Sn(NCS)_2 \cdot \text{bipyridine}$ show two bands due to the NC stretching vibrations (24). This indicates probable *cis* coordination of the two NCS groups.

K. $[(CH_3)_3SnX_2]^-$, $[(CH_3)_2SnX_4]^{2-}$, and $[CH_3SnX_5]^{2-}$ ($X = \text{halogen or NCS}$)

Halide anions are also Lewis bases, and are known to act as donors to give complex organotin salts, $M^+[(CH_3)_3SnX_2]^-$, $M_2^+[(CH_3)_2SnX_4]^{2-}$, or

$M_2^+[(CH_3)_3SnX_3]^{2-}$ (62–65). A halogen-bridged, dimeric structure was first proposed for the anion $[(CH_3)_3SnBr_2]^-$ upon the assumption that tin could assume only tetrahedral or octahedral configurations (63). However, in the infrared spectrum of the tetramethylammonium salt of $[(CH_3)_3Sn(NCS)_2]^-$, there was no band due to the symmetric SnC_3 stretching vibration (24). Therefore, a planar SnC_3 arrangement and a bipyramidal structure is expected.

Wilkins and Heandler reported a comparative investigation of the infrared spectra of dimethyltin fluoride complexes and of inorganic tin fluoride complexes (64). As in the case of other complex metal halides, the spectra of most of the tin complexes in the $Sn-F$ stretching region ($620-540\text{ cm}^{-1}$) fall into two classes, the numbers of absorption bands being characteristic of *cis* and *trans* configurations. The spectra of the ionic compounds containing $[(CH_3)_2SnF_4]^{2-}$ anion correspond to the *trans* configuration class and since the spectra show no appropriate band assignable to the symmetric $Sn-C$ stretching vibration, the *trans* configuration has been assumed for this anion.

The absence of the band due to the symmetric $Sn-C$ stretching vibration and the appearance of only one band in the $N-C$ stretching region in the spectrum of $[(CH_3)_4N]_2^+ \cdot [(CH_3)_2Sn(NCS)_4]^{2-}$ also indicate a *trans* octahedral configuration for the anion (24).

L. $R_3Sn(ox)$

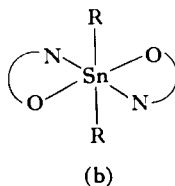
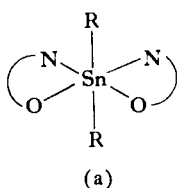
The ultraviolet absorption spectrum of $(C_6H_5)_3Sn(ox)$ in 95% ethanol showed absorptions identical with those of 8-hydroxyquinoline. The investigators (27) took this to mean that no chelation occurred in this compound. However, this observation is inconsistent with the fact that $(C_6H_5)_3Sn(ox)$ has a yellow color, while 8-hydroxyquinoline in the pure state is a colorless compound. In a more recent study (66) of this compound, the spectrum in cyclohexane solution showed a ligand band at about $370\text{ m}\mu$ with a long tailing toward the visible region. This absorption band position corresponds to those of various chelated metal oxinates at $370-430\text{ m}\mu$, rather than to that of 8-hydroxyquinoline, which occurs at about $320\text{ m}\mu$ in cyclohexane. This observation, together with the results of molecular weight determinations, indicate that the compound has a chelate structure with a pentacoordinated tin atom. Analogous results have been obtained for

$(\text{CH}_3)_3\text{Sn}(\text{ox})$ and $(n\text{-C}_4\text{H}_9)_3\text{Sn}(\text{ox})$, which are also believed to have pentacoordinate chelated structures (40).

M. $\text{R}_2\text{Sn}(\text{ox})_2$

Several reports dealing with the properties of dialkyltin dioxinates have been published in recent years (27–30, 33). The compounds are yellow crystals and, unlike the simple alkoxides $\text{R}_2\text{Sn}(\text{OR}')_2$, are stable to moisture. The ultraviolet absorption spectra of $\text{R}_2\text{Sn}(\text{ox})_2$ compounds are very similar to those of other metal oxinates (27, 28). In addition, the molecular extinction coefficient around $380\text{ m}\mu$ of $\text{R}_2\text{Sn}(\text{ox})_2$ is about twice that of 8-hydroxyquinoline at about $315\text{ m}\mu$. From these observations these tin oxinates are assumed to be chelate compounds with hexacoordinated tin atoms.

Assuming the usual octahedral geometry for this coordination number, both geometrical and optical isomers might be expected (28). Nelson and Martin attempted to resolve such compounds by chromatographic techniques using D-lactose (33). However, they observed only a single elution peak, and concluded that only the *trans* isomer was present in solution. This conclusion is in accord with the general tendency of hexacoordinated dialkyltin derivatives to assume a *trans* alignment of the two alkyl groups. There are still two possibilities for the configuration, as shown below. Configuration (a) is composed of *cis* alignments of two nitrogen and two oxygen atoms, whereas configuration (b) has all *trans* alignments. The dipole moment of $(\text{C}_6\text{H}_5)_2\text{Sn}(\text{ox})_2$ was observed to be 4.6 D (33). This seems to favor the *cis* configurations (a).



McGrady and Tobias have found tin-proton spin-spin coupling constants of 67.9 cps ($J_{\text{Sn}117\text{CH}}$) and 71.2 cps ($J_{\text{Sn}119\text{CH}}$) for $(\text{CH}_3)_2\text{Sn}(\text{ox})_2$ (30). These values are comparable to those found for tetrahedrally coordinated tin compounds, rather than those for linear dimethyltin groups. These

results were interpreted as indicating that the *s* character in the tin bonding orbitals is distributed not only to two Sn—C bonds but also to the tin-oxinate bondings, probably to the two tin-oxygen bonds.

The infrared spectra of $R_2Sn(ox)_2$ compounds are very complicated due to the absorption bands of the oxinato ligand. Hence, little information of value for the structure has been obtained from the infrared spectra.

N. $XR_2Sn(ox)$

Compounds of this type have been reported independently by two groups (66, 67). The compounds are stable yellow crystals when pure, but disproportionate into R_2SnX_2 and $R_2Sn(ox)_2$ in moist solution. From procedures analogous to those used to study $R_3Sn(ox)$ and $R_2Sn(ox)_2$, described above, these compounds were found to contain, when X is monodentate, a pentacoordinated tin atom chelated by an oxinato ligand. In the ultraviolet spectra of these compounds, the appropriate absorption peak occurs at even longer wavelengths than that observed for $R_3Sn(ox)$ and $R_2Sn(ox)_2$.

O. $R_2Sn(acac)_2$

The infrared spectrum of $(CH_3)_2Sn(acac)_2$ shows only the antisymmetric stretching vibration of the SnC_2 moiety near 560 cm^{-1} . The symmetric vibration is observed near 510 cm^{-1} in the Raman spectrum (30–32). Therefore the two methyl groups in this compound may occupy *trans* positions with respect to the central tin atom. The absorption bands due to the acetylacetonato ligand of this compound occur at analogous frequencies to those of copper acetylacetonate.

McGrady and Tobias studied the proton NMR spectra of several dimethyltin bis chelates (32). No splitting of the ring methyl proton signal could be observed in the spectra for $(CH_3)_2Sn(acac)_2$. The proton coupling constants, $(J_{Sn117CH})$ and $(J_{Sn119CH})$, for $(CH_3)_2Sn(acac)_2$ are intermediate between the values for the aquo, and hydroxo complexes of the dimethyltin cation, both of which have the *trans* structure. These facts give strong support to the postulated *trans* structure for the compound.

P. $RSn(OOCR')_3$ and $C_6H_5Sn(tropolonato)_3$

The infrared spectra of $RSn(OOCR')_3$ compounds indicate the non-existence of an ester-type carboxyl group (68). Supposing chelate-type

bondings between the tin and each carboxylate group, as have been assigned to $R_2Sn(OOCR')_2$, the tin atom would be heptacoordinated.

Phenyltin trichloride and tropolone yield $C_6H_5Sn(tropolonato)_2Cl$, which is converted to $C_6H_5Sn(tropolonato)_3$ by reaction with the sodium salt of tropolone (69). The molecular weight of the compound in dichloromethane is that of a monomer, and a heptacoordinated structure of tin has been proposed.

IV

ORGANOSTANNOXANES

A. Introduction

It is well known that the chemistry of organosiloxanes is distinguished from that of the carbon ethers in that the $Si-O-Si$ linkage has the peculiar $d_\pi-p_\pi$ bonding which greatly influences the physical and chemical properties of the siloxanes. During the last few years knowledge of the chemistry of the organostannoxanes has been accumulated. These compounds show unique properties associated with the $Sn-O-Sn$ linkage which distinguish the chemistry of the organostannoxanes from that of the organosiloxanes.

A review published in 1960 includes organostannoxanes of the types $R_3SnOSnR_3$, polymeric R_2SnO , $RSnOOH$, and several complex compounds formed from R_2SnO and R_2SnX_2 ($X = \text{halogens, } OOCCH_3$) (1). Recent investigations have been concerned mainly with the last type of compound, since this type of compound has been isolated most often during the course of experimental work.

These types of complex compounds are distinguished, in this article, as Type A for the compounds of composition $R_4Sn_2X_2O$, and as Type B for the compounds of composition $R_4Sn_2XO(OH)$. The Type A compounds have been obtained by reaction of R_2SnX_2 and polymeric R_2SnO in 1:1 mole ratio. The Type B compounds can be isolated when the dihalide and oxide react in 1:3 mole ratio. These compounds are usually stable, highly crystalline, and soluble in organic solvents. Pfeiffer and Brach in 1914 assumed that the Type A compounds had the formula $XR_2SnOSnR_2X$ (70). However, in a series of papers, Harada argued the case for $R_2SnO \cdot R_2SnX_2$ and for a cyclic trimeric structure, with each of the three tin atoms having coordination number four or five (71).

Recently, evidence has accumulated in support of the initial formulation by Pfeiffer. Okawara and Rochow prepared a compound of type A with $R = \text{CH}_3$ and $X = \text{Cl}$ by the partial hydrolysis of $\text{Cl}(\text{CH}_3)_2\text{Sn}(\text{OOCH})$ or of $\text{Cl}(\text{CH}_3)_2\text{Sn}(\text{OOCCH}_3)$, and by the reaction of polymeric $(\text{CH}_3)_2\text{SnO}$ suspended in methanol with aqueous HCl (72). They suggested the distannoxane formula, $\text{Cl}(\text{CH}_3)_2\text{SnOSn}(\text{CH}_3)_2\text{Cl}$, for this compound. An observation in support of this formulation is that this compound has the characteristic strong absorption associated with the $\text{Sn}-\text{O}-\text{Sn}$ bond near 600 cm^{-1} , analogous to the absorption found in the infrared spectra of polymeric SnO_2 , $\text{CH}_3\text{SnO}_{3/2}$, and $(\text{CH}_3)_2\text{SnO}$ (73). At the same time Gibbons *et al.*, mentioned independently that " $(\text{C}_4\text{H}_9)_2\text{SnO} \cdot (\text{C}_4\text{H}_9)_2\text{SnCl}_2$ " should be represented as $\text{Cl}(\text{C}_4\text{H}_9)_2\text{SnOSn}(\text{C}_4\text{H}_9)_2\text{Cl}$, because the compound can be obtained by adding water to the ethanol solution of $(\text{C}_4\text{H}_9)_2\text{SnCl}_2$ or by the oxidation of the ditin compound, $\text{Cl}(\text{C}_4\text{H}_9)_2\text{SnSn}(\text{C}_4\text{H}_9)_2\text{Cl}$, by oxygen (74).

TABLE III
TYPE A COMPOUNDS, $\text{XR}_2\text{SnOSnR}_2\text{X}$

X	R	References ^a
$\text{OSi}(\text{CH}_3)_3$	$\text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}_4\text{H}_9$	76
F	C_4H_9	77
Cl	$\text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}_4\text{H}_9$	72, 75, 77
Br	$\text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}_4\text{H}_9$	75, 77
NCS	$\text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}_4\text{H}_9$	77, 78
NCO	$\text{CH}_3, \text{C}_4\text{H}_9, \text{C}_6\text{H}_5$	79, 80
OOCR'^b	$\text{CH}_3, \text{C}_4\text{H}_9$	72, 77, 81
OC_6H_5	$\text{CH}_3, \text{C}_4\text{H}_9$	81-83
$\text{OC}_6\text{H}_4\text{Y}^c$	$\text{CH}_3, \text{C}_4\text{H}_9$	81, 83
Camphorsulfoxy	C_2H_5	77
β -Naphthoxy	C_4H_9	83
α -Nitroso- β -naphthoxy	$\text{CH}_3, \text{C}_2\text{H}_5$	84
OOR		85

^a Representative reports are cited.

^b $\text{R}' = \text{CH}_3$ (72), H , C_2H_5 , C_3H_7 , CH_2Cl , CHCl_2 , CCl_3 , CH_2Br , $\text{CH}_2(\text{CN})$ (81) for $\text{R} = \text{CH}_3$; $\text{R}' = \text{CH}_3, \text{C}_6\text{H}_5$ (77) for $\text{R} = \text{C}_4\text{H}_9$.

^c $\text{Y} = \text{OCH}_3(o-)$ (81) for $\text{R} = \text{CH}_3$; $\text{Y} = \text{OCH}_3(p-)$, $\text{tert-C}_4\text{H}_9(p-)$, $\text{NO}(p-)$ (83) for $\text{R} = \text{C}_4\text{H}_9$.

The partial hydrolysis of the Type A compounds gives the corresponding hydroxides, $\text{XR}_2\text{SnOSnR}_2\text{OH}$, the physical properties of which are found to be identical with those of Type B compounds (75). At the same time the compounds formerly represented as $\text{R}_2\text{SnO} \cdot \text{R}_2\text{SnX}(\text{OH})$ or $\text{R}'(\text{R}_2\text{SnO})_3\text{OR}' \cdot \text{R}_2\text{SnX}_2$ have been found to be analogous to the distannoxanes. To date, there are a wide range of compounds known having compositions of Type A or B. These are summarized in Tables III and IV.

TABLE IV
TYPE B COMPOUNDS, $\text{XR}_2\text{SnOSnR}_2\text{OH}^a$

X	R	References
Cl	$\text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}_4\text{H}_9$	75, 86
Br	$\text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}_4\text{H}_9$	75
I	$\text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}_4\text{H}_9$	75
NCS	$\text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}_4\text{H}_9$	78
NCO	$\text{C}_4\text{H}_9, \text{C}_6\text{H}_5$	80
OOCCH_3	C_4H_9	77, 86

^a Additional compounds: $(\text{CH}_3)_2\text{SnO} \cdot (\text{CH}_3)_2\text{SnCrO}_4$, $(\text{CH}_3)_2\text{SnO} \cdot (\text{CH}_3)_2\text{Sn}(\text{succinato})_2$, $(\text{CH}_3)_2\text{SnO} \cdot (\text{CH}_3)_2\text{Sn}[\text{Fe}(\text{CN})_6]$ (79). Tetrapropyl- and tetrabutyl-1-(α -nitroso- β -naphthoxy)-3-chlorodistannoxanes (84). Tetra-*o*-phenoxyphenyl-1,3-dihydroxydistannoxane (87).

B. The Dimeric Structure and Properties of $\text{XR}_2\text{SnOSnR}_2\text{X}$ and $\text{XR}_2\text{SnOSnR}_2\text{OH}$

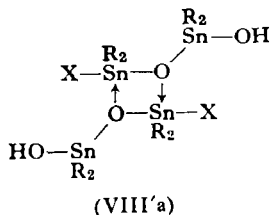
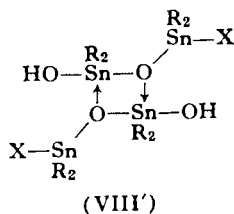
An X-ray crystal study of a Type A compound, $(\text{CH}_3)_3\text{SiO}(\text{CH}_3)_2\text{-SnOSn}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_3$, showed a dimeric structure containing a four-membered ring due to reciprocal coordination of an oxygen atom between two tin atoms of one molecule to a tin atom of the other molecule, as is shown in structure (VIII) (Section II, A), where R and X represent CH_3 and $\text{OSi}(\text{CH}_3)_3$ groups, respectively (4).

Molecular weight determinations also show that soluble compounds of both Types A and B are dimeric in solution (4, 75, 77, 78, 82, 83, 87, 88). On the other hand, compounds of the type $\text{R}_3\text{SnOSnR}_3$, as well as R_2SnX_2 , are monomeric in benzene (75). A sulfide analogous to Type A molecules,

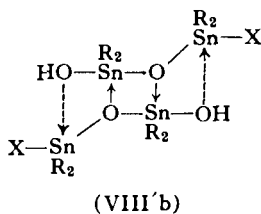
$\text{Cl}(\text{C}_4\text{H}_9)_2\text{SnSSn}(\text{C}_4\text{H}_9)_2\text{Cl}$, is monomeric in benzene (89). From these observations, it can be concluded that the dimerization of A and B type compounds is associated with the $\text{Sn}-\text{O}-\text{Sn}$ linkage, and that the important factor in the dimerization is the presence of an anionic ligand, X, attached to the tin atoms.

In the dimeric structure of Type A distannoxanes, there are both tetra-coordinated and pentacoordinated tin atoms, and accordingly, two different kinds of substituents, X. This difference is evident in the reaction of $\text{XR}_2\text{SnOSnR}_2\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) with an excess of organic base, such as pyridine. One of the two substituents is selectively replaced, with the formation of a corresponding Type B compound (75). The ^{119}Sn nuclear magnetic resonance spectra of $\text{Cl}(\text{C}_4\text{H}_9)_2\text{SnOSn}(\text{C}_4\text{H}_9)_2\text{Cl}$ and of $\text{Br}(\text{C}_4\text{H}_9)_2\text{SnOSn}(\text{C}_4\text{H}_9)_2\text{Br}$ indicate the existence of tin atoms in two different environments (77, 89). The proton magnetic resonance spectra of $\text{Cl}(\text{CH}_3)_2\text{SnOSn}(\text{CH}_3)_2\text{Cl}$ (77) and $(\text{CH}_3)_3\text{SiO}(\text{CH}_3)_2\text{SnOSn}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_3$ (90) show the presence of equal amounts of two types of methyl groups attached to tin in both cases, and to silicon in the latter compound. The NMR spectra obtained at various temperatures of the trimethylsiloxy compound revealed that the dimer dissociates in solution at higher temperatures (90). From the equilibrium constants obtained at several temperatures the strength of the tin-oxygen coordinate bond was estimated as 4.5 kcal/mole. Further evidence for dissociation at higher temperatures is the fact that in the determination of the molecular weight of $(\text{C}_6\text{H}_5\text{O})(\text{C}_4\text{H}_9)_2\text{SnOSn}(\text{C}_4\text{H}_9)_2(\text{OC}_6\text{H}_5)$ by the Rast method a value corresponding to the monomer was obtained (83). On the other hand, in carbon tetrachloride solution at 37.5° , molecular weight determination indicated that the compound was dimeric.

From the infrared absorption due to the $\text{SnO}-\text{H}$ stretching vibration of the Type B compounds ($\text{X} = \text{halogens}$), the presence of hydrogen bonds can not be assumed in these compounds (75). These hydroxides are stable against condensation by loss of water even at high temperatures below the



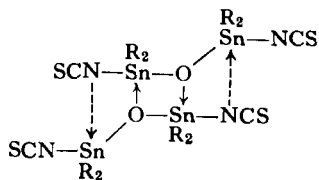
melting point (75). There are two probable configurations for the dimeric structure of Type B compounds, as shown in (VIII') and (VIII'a). The configuration (VIII') contains the hydroxyl group on the pentacoordinated tin atom, while in the configuration (VIII'a) the hydroxyl group is on the tetracoordinated tin atom. The structure (VIII') is favored upon the assumption that, in the partial hydrolysis process from Type A compounds, the tin atom which most easily undergoes substitution would be the pentacoordinated one (75). Further, the existence of a stable hydroxyl group may be attributed to additional coordination from the hydroxyl oxygen to the tetracoordinated tin atom similar to that occurring in dimeric $(\text{CH}_3)_3\text{SnOH}$ (56). This hypothetical, ladder type-structure (VIII'b) has been used



to explain the infrared spectra of $(\text{SCN})\text{R}_2\text{SnOSnR}_2(\text{NCS})$ and $(\text{SCN})\text{R}_2\text{SnOSnR}_2\text{OH}$ (24, 78). In the infrared spectra of $(\text{SCN})\text{R}_2\text{SnOSnR}_2(\text{NCS})$, two bands due to the NC stretching vibration are observed near 2040 cm^{-1} and 1960 cm^{-1} . The NC stretching band at 1960 cm^{-1} is unique since a band at such a low frequency has never been observed in the spectra of other alkyltin isothiocyanates nor in the spectra of transition metal isothiocyanates. Assuming that the isothiocyanate exists as a resonance hybrid of (a) and (b), this lowering of the NC stretching band frequency may be inter-



preted as due to an increased contribution of form (b). The contribution from (b) indicates the occurrence of nitrogen bridging between two tin atoms, as shown below.



In the spectra of $(\text{SCN})\text{R}_2\text{SnOSnR}_2\text{OH}$ the band at 1960 cm^{-1} is absent. This indicates that a hydroxyl group has replaced a bridging NCS group.

The postulate of dimerization to such a ladder-type structure can also explain the presence of two bands in the infrared spectrum of $(\text{CH}_3)_3\text{SiOR}_2\text{SnOSnR}_2\text{OSi}(\text{CH}_3)_3$ at 980 cm^{-1} and 910 cm^{-1} (76). These are assigned to vibrations of nonbridging and bridging $(\text{Sn}-)\text{O}-\text{Si}(\text{CH}_3)_3$

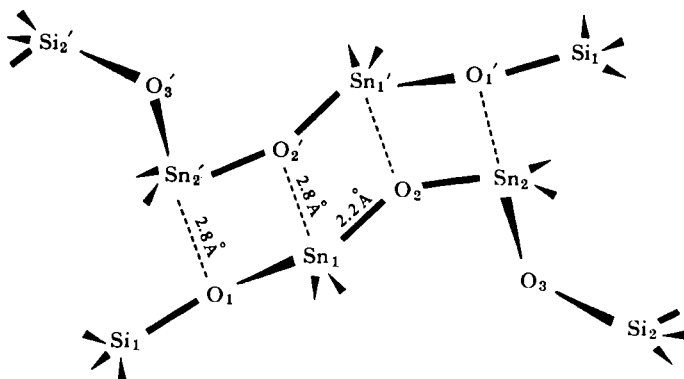


FIG. 4. Crystal structure of $[(\text{CH}_3)_3\text{SiO}(\text{CH}_3)_2\text{SnOSn}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_3]_2$.

groups, respectively. The fact that the infrared spectra of monomeric $\text{R}_3\text{SnOSi}(\text{CH}_3)_3$ shows only the band near 980 cm^{-1} (91) supports this assignment.

The ladder-type structure has recently been confirmed by an X-ray study of $(\text{CH}_3)_3\text{SiO}(\text{CH}_3)_2\text{SnOSn}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_3$ (92). The structure is shown in Fig. 4.

Stable iodides of Type A distannoxanes have not been isolated. The alkyl compounds, $\text{R}_3\text{SnOSnR}_3$, are monomeric. These observations may be explained as due to the lack of ability of iodine or an alkyl group to give stable ladder-type distannoxane structures.

C. Polymeric Organotin Oxides

Although the polymeric oxides are amorphous in appearance, X-ray powder photographs indicate a fairly ordered intermolecular arrangement (93). There is no doubt that the distannoxane ring would be present in these polymeric oxides. However, such an oxide could contain only penta-coordinated or both tetra- and pentacoordinated tin. From the results of

Mössbauer spectroscopy, Gol'danskii *et al.* have concluded that the tin atoms have a coordination number of five (94). This would indicate that all of the tin atoms in the oxide are included in four-membered Sn—O rings (86, 90, 95–98).

ACKNOWLEDGMENTS

The authors express their thanks to Dr. C. R. Dillard, Fulbright Research Professor at Osaka University, 1965–1966, for assistance in improving the manuscript.

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Organometallic Pseudohalides

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I. Introduction	169
II. Methods of Preparation	171
A. Syntheses from Pseudohalide Salts	171
B. Syntheses from Covalent Pseudohalides	172
C. Other Methods of Synthesis	174
III. Structure and Physical Properties	175
A. Trends in Melting and Boiling Points	175
B. Thermal Stability and Decomposition	175
C. Infrared Spectra	177
D. Ultraviolet Spectra	179
IV. Structural Isomerism and Chemical Bonding	181
A. (Iso)Cyanides	181
B. (Iso)Cyanates	186
C. (Iso)Thiocyanates and (Iso)Selenocyanates	187
D. Fulminates	189
E. Bonding in Derivatives of Triatomic Pseudohalides	189
V. Chemical Properties	193
A. Solvolyses	193
B. Exchange Reactions and the Conversion Series	193
C. Other Displacement Reactions	194
D. Donor-Acceptor Complexes	195
E. Additions to the Pseudohalide Group	199
VI. Tables of Properties	200
References	219

I

INTRODUCTION

The terms *pseudohalogen* and *pseudohalide* were first suggested by Birckenbach and Kellerman to describe polyatomic groups resembling

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TABLE I
PSEUDOHALIDE GROUPS

Name	"Normal" Form	"Iso" Form
Cyanide	-CN	-NC
Cyanate	-OCN	-NCO
Thiocyanate	-SCN	-NCS
Selenocyanate	-SeCN	-NCSe
Fulminate	-CNO	(-ONC)
Azide	-NNN	—

halogens and halides in their chemical properties (1). In this review, we will consider organometallic derivatives of the diatomic and triatomic pseudohalide groups listed in Table I: (iso)cyanide, (iso)cyanate, (iso)thiocyanate, (iso)selenocyanate, azide, and fulminate.² The fulminate group, -CNO, although not usually classified as a pseudohalogen, is included because of its marked halogenoid character and strong resemblance to the other pseudohalogens, particularly the isomeric cyanate. The numerous pseudohalide derivatives of the transition metals are best considered as metal complexes and will not be treated in this review. Exception will be made, however, for the few organogold and organoplatinum pseudohalides, which differ markedly from transition metal complexes and resemble main group pseudohalides in their properties.

The first organometallic pseudohalide reported was cacodyl cyanide, $(\text{CH}_3)_2\text{AsCN}$, which Bunsen called "this beautiful but unbelievably toxic compound" (2). Since that time, about 350 compounds falling under the scope of this review have been reported. In recent years the pace of research on organometallic pseudohalides has quickened, with increasing attention given to structural and bonding problems; these will be emphasized in this review. To a first approximation, many properties of the covalent pseudohalide groups are relatively independent of the attached organometallic residue, making them particularly appropriate for broad comparative studies. The properties of organometallic pseudohalides as a class have not been systematically compared, but reviews on organometallic azides (3) and on pseudohalides of Group III and IV elements (4) have appeared.

² The use of iso in parentheses will designate a compound in which the point of attachment to the pseudohalide group is indeterminate [e.g., (iso)cyanate]. When the point of attachment is to be indicated, specific terms will be used (e.g., cyanate, isocyanate). See Table I.

II

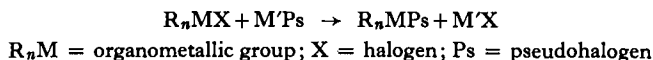
METHODS OF PREPARATION

The various reported synthetic methods for organometallic pseudohalides are outlined below. Most of them involve reaction of previously formed pseudohalogen derivatives with organometallic substrates; these are classified in Sections A and B by type of pseudohalogenating agent used. Miscellaneous reactions, mostly limited in scope, are collected under Section C. Numbers of the subsections describing synthetic methods are keyed to Tables X–XV, which list the known organometallic pseudohalides and their physical properties.

A. Syntheses from Pseudohalide Salts

1. Alkali Metal Pseudohalides in Nonaqueous Solvents

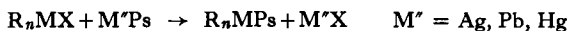
This is the single most commonly used preparative method, and is extensively employed for preparation of moisture-sensitive derivatives of B, Si, and As. Li, Na, and K salts have all been reported as satisfactory starting materials. The reaction is summarized by the equation



Many solvents have been used as reaction media—acetonitrile, pyridine, benzene, and tetrahydrofuran being perhaps the most common. The solvent can be chosen to allow easy separation by fractional distillation. In a few cases, the pseudohalide may be prepared by direct reaction, omitting the solvent. Anhydrous $AlCl_3$ has been reported as a good catalyst for the azidization of organosilyl halides by this reaction (5–8); an aluminum azide may be the actual azidizing agent.

2. Heavy Metal Pseudohalides in Nonaqueous Solvents

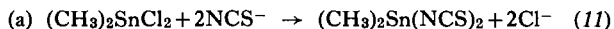
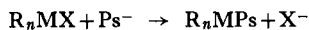
A variation of the above method involves the use of heavy metal pseudohalides as the reactive material. Silver salts have been most frequently used, but the pseudohalides of lead and mercury have also been employed. As in the method described above (Section II, A, 1), the organometallic compound must have a labile bond.



In most cases, organometallic halides are used, but there have been a few reports of metal-hydrogen bonds being employed (9, 10). Diethyl ether has usually been used as a solvent. The greater reactivity and covalent nature of the heavy metal pseudohalides, as compared to the alkali metal analogs, make reactions possible at room temperature or below; the major disadvantage is the photosensitivity and shock sensitivity of these salts, particularly the azides and fulminates. This method employing heavy metal pseudohalides is general for all pseudohalogen groups.

3. *Pseudohalide Ions in Solution*

For the rather small number of organometallic halides that form stable aqueous solutions (mostly derivatives of the heavier metals, such as Tl, Sn, Pb) water is a convenient reaction medium.

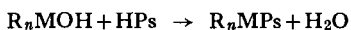


Complete reaction can be ensured by addition of excess pseudohalide ion. The product may be isolated by precipitation (if insoluble) or by extraction with an organic solvent immiscible with water, such as diethyl ether.

B. *Syntheses from Covalent Pseudohalides*

1. *Hydrogen Pseudohalides and Organometallic Hydroxides*

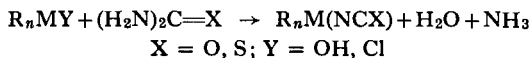
The most commonly used covalent pseudohalogenating agents are the hydrogen derivatives, HPs. These are acidic in nature and react with basic organometallic hydroxides or oxides.



Reaction conditions will depend on the basic character of the hydroxide; derivatives of B and Si do not react at all, while weakly acidic derivatives, such as the Ge hydroxides, require an excess of acid (8, 13). Two-phase systems (e.g., ether-water), appear to be the most successful. The reaction has been used for derivatives of Tl, Ge, Sn, Pb, Sb, and Bi.

2. *Fusion with Urea or Thiourea*

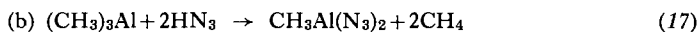
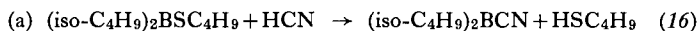
Recently it has been reported that organometallic hydroxides give (iso)cyanates or (iso)thiocyanates when melted with urea or thiourea, respectively (14).



At the reaction temperature urea and thiourea are known to undergo decomposition to HNCO and HNCS, respectively, which are probably the actual species reacting with $R_n\text{MOH}$. The method has been used so far to prepare derivatives of Sn (14), As (14), and Si (15).

3. Hydrogen Pseudohalides and Other Organometallics

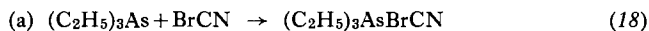
In cases where the hydroxide is unsuitable as starting material, other organometallic substrates containing acid-sensitive bonds may be used.



This reaction is generally more sensitive than the method of Section II, B, 1, and requires the exclusion of moisture and air.

4. Pseudohalogens and Organometallics

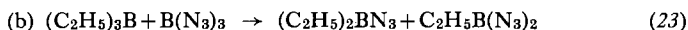
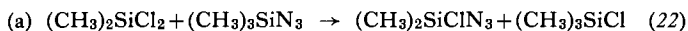
Free pseudohalogens and pseudohalides have been found to react with organometallics of low valence metals to give pseudohalide derivatives.



Most of these examples use cyanogen and its derivatives as the pseudohalogenating agent. There have been recent reports of the use of ClN_3 to prepare inorganic and organometallic azides by this method (20, 20a, 21).

5. Pseudohalide Exchange Reactions

A number of organometallic pseudohalides have been prepared by halogen-pseudohalogen or alkyl-pseudohalogen exchange reactions.

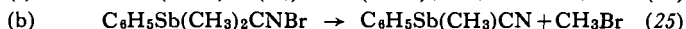
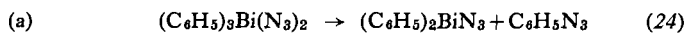


The equilibrium can be forced to one side by removal of the most volatile component. This reaction is particularly good for making compounds having both halogens and pseudohalogens bonded to the metal.

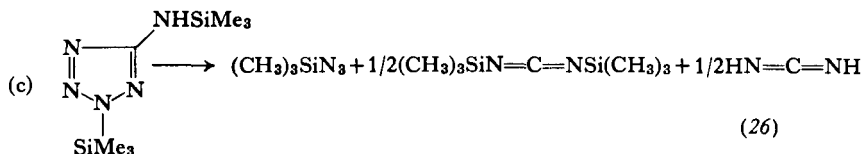
C. Other Methods of Synthesis

1. Pyrolysis

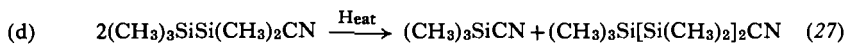
Pyrolysis of organopolypseudohalides of Sb(V) and Bi(V) will yield other pseudohalides.



A tetrazole derivative has been reported to give $(CH_3)_3SiN_3$ when heated.

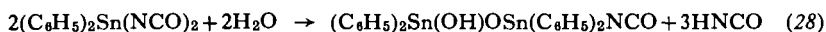


Pentamethylcyanodisilane, when heated to 115°–130° C, rearranges into trimethylcyanosilane and permethylpolysilanes of various chain length.



2. Hydrolysis

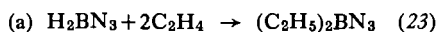
Partial hydrolysis of organometallic polypseudohalides of Sn, Sb, and Bi gives oxy or hydroxy derivatives.



This reaction is probably quite general.

3. Addition

Only two examples are presently known of the synthesis of organometallic pseudohalides by addition reactions. Azidoborane has been shown to add across the double bond of olefins.



Organometallic cyanides of Group IV elements will react with sulfur to form isothiocyanates.



Both reactions are probably general.

III

STRUCTURE AND PHYSICAL PROPERTIES

A. Trends in Melting and Boiling Points

Physical properties of the known organometallic pseudohalides are summarized in Tables X–XV. In general, melting and boiling points follow the predictions given in Rochow *et al.* (31). The differences that appear arise from the basic properties and/or the polyatomic nature of the pseudohalide groups. Physical properties depend on the nature of the metal, the pseudohalide residue, and the organic group. Trends can be summarized as follows:

1. *Change of Metal.* Within a given periodic group, melting and boiling points increase as the atomic weight of the metal increases, while solubility in nonpolar solvents decreases. Changes are usually, though not always, gradual and continuous.

2. *Change of Pseudohalogen.* In a given compound, substitution of a pseudohalide group for an alkyl group decreases the volatility, while substitution for an aryl group increases the volatility. Thermal stability tends to decrease as the number of pseudohalogen groups on a metal increases. Boiling points of analogous compounds usually vary in the order $CN > NCS > CNO > N_3 \sim NCO$. Not enough data are available to place the selenocyanates in this series, but they appear to be less volatile than the thiocyanates.

3. *Change of Organic Group.* For a homologous series, increasing chain length in straight-chain alkyls causes the boiling point to increase steadily, and the melting point to decrease until about C_5 , when it levels off. Branched-chain organometallics tend to be more volatile than their straight-chain analogs. Aryl organometallic pseudohalides are less volatile and more stable thermally than their alkyl analogs.

B. Thermal Stability and Decomposition

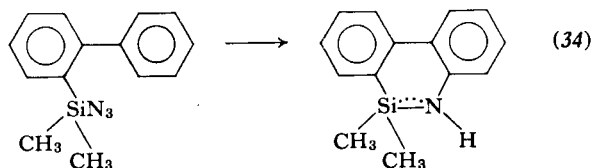
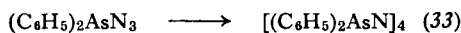
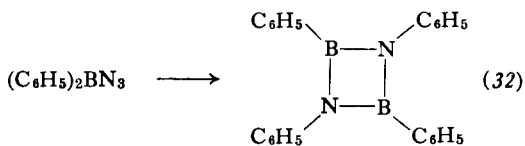
Only for azides and fulminates have serious thermolysis studies been carried out; both classes of compounds show surprising stability. Table II lists temperatures at which rapid decomposition ensues for a number of pseudohalides.

TABLE II

DECOMPOSITION TEMPERATURES ($^{\circ}\text{C}$) OF SOME ORGANOMETALLIC PSEUDOHALIDES

<i>Azides</i>		<i>Selenocyanates</i>	
$(\text{C}_6\text{H}_5)_2\text{BN}_3$	100 $^{\circ}$	$\text{C}_6\text{H}_5\text{HgSeCN}$	100 $^{\circ}$
$(\text{C}_6\text{H}_5)_3\text{SiN}_3$	380 $^{\circ}$	$(\text{C}_6\text{H}_5)_2\text{BiSeCN}$	25 $^{\circ}$
$(\text{C}_6\text{H}_5)_2\text{Si}(\text{N}_3)_2$	320 $^{\circ}$	<i>Cyanides</i>	
$(\text{C}_6\text{H}_5)_3\text{GeN}_3$	375 $^{\circ}$	$(\text{CH}_3)_2\text{AlCN}$	100 $^{\circ}$
$(\text{C}_6\text{H}_5)_2\text{AsN}_3$	191 $^{\circ}$	$(\text{CH}_3)_5\text{Si}_2\text{CN}$	175 $^{\circ}$
$(\text{C}_6\text{H}_5)_3\text{SnN}_3$	300 $^{\circ}$	$(\text{CH}_3)_2\text{C}_6\text{H}_5\text{SbBrCN}$	150 $^{\circ}$
$(\text{C}_6\text{H}_5)_2\text{SbN}_3$	200 $^{\circ}$	$(\text{iso-C}_3\text{H}_7)_2\text{AuCN}$	121–133 $^{\circ}$
CH_3HgN_3	200 $^{\circ}$	$(\text{C}_6\text{H}_5)_2\text{TlCN}$	318 $^{\circ}$
$\text{C}_6\text{H}_5\text{Tl}(\text{N}_3)_2$	200 $^{\circ}$	$(\text{C}_6\text{H}_5)_3\text{PbCN}$	250 $^{\circ}$
$(\text{C}_6\text{H}_5)_3\text{PbN}_3$	185 $^{\circ}$	<i>Cyanates</i>	
$(\text{C}_6\text{H}_5)_3\text{Bi}(\text{N}_3)_2$	100 $^{\circ}$	$(\text{CH}_3)_2\text{AlCN}$	100 $^{\circ}$
<i>Fulminates</i>		$(n\text{-C}_4\text{H}_9)_3\text{Sb}(\text{NCO})_2$	190 $^{\circ}$
$(\text{C}_6\text{H}_5)_3\text{SiCNO}$	105 $^{\circ}$	$(\text{CH}_3)_3\text{PbNCO}$	220 $^{\circ}$
$(\text{C}_6\text{H}_5)_3\text{GeCNO}$	122 $^{\circ}$	<i>Thiocyanates</i>	
$(\text{C}_6\text{H}_5)_3\text{SnCNO}$	146–148 $^{\circ}$	$(\text{C}_2\text{H}_5)_3\text{SnNCS}$	282 $^{\circ}$
$\text{C}_6\text{H}_5\text{HgCNO}$	178 $^{\circ}$	$(\text{CH}_2=\text{CH})_2\text{Sn}(\text{NCS})_2$	164 $^{\circ}$
$(\text{C}_6\text{H}_5)_2\text{TlCNO}$	290 $^{\circ}$	$(\text{C}_6\text{H}_5)_3\text{PbNCS}$	230 $^{\circ}$
$(\text{C}_6\text{H}_5)_3\text{PbCNO}$	174 $^{\circ}$		

Among organometallic azides, those of Group IV metals are the most inert, having decomposition temperatures markedly higher than those of organic azides (3). In these compounds, thermal stability decreases with increasing atomic weight of the metal. The azides of B, Si, Ge, and As decompose by internal cleavage of the N_3 group and loss of nitrogen, giving



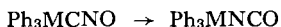
metal–nitrogen polymers, in which migration of an organic group from metal to nitrogen apparently occurs. In several cases discrete products have been obtained.

Azides of more electropositive metals decompose by breaking the metal–nitrogen bond, losing all of their nitrogen on heating.



Organometallic azides generally lack the shock sensitivity which is characteristic of simple alkyl azides and of many inorganic metal azides. Even compounds containing several N_3 groups on a single metal atom are insensitive to shock, e.g., $(\text{C}_6\text{H}_5)_2\text{Si}(\text{N}_3)_2$ (3).

Most of the organometallic fulminates are also not shock sensitive, although $(\text{C}_3\text{H}_7)_3\text{PbCNO}$ and $(\text{C}_2\text{H}_5)_2\text{TlCNO}$ are reported to be explosive. When Group IV triphenylmetal fulminates are heated, they rearrange at the temperatures shown in Table II to the isomeric (iso)cyanates (36).



The mechanism of this interesting reaction is unknown. Surprisingly, the temperature of rearrangement *increases* in the order $\text{Si} < \text{Ge} < \text{Sn} < \text{Pb}$.

C. Infrared Spectra

All pseudohalogen compounds have a strong infrared absorption band in the $2000\text{--}2300\text{ cm}^{-1}$ region, which may be considered as diagnostic for such compounds. This band arises from the C—N stretching mode in the (iso)cyanides, and from the asymmetric stretching mode in the other pseudohalides. Three-atom pseudohalogen groups have three vibrational fundamentals: a deformation mode, and asymmetric and symmetric stretching vibrations.³ Table III lists pseudohalogen vibrational frequencies which have been observed for organometallic derivatives. Except for azides, the table is essentially complete for all organometallic pseudohalides whose spectra have been carefully studied. A complete table of infrared spectra for organometallic azides appears in Thayer (3).

Although the asymmetric stretching frequency varies remarkably little from one pseudohalide to another, the position of symmetric stretching and deformation modes depends greatly on the nature of the pseudohalogen. In

³ The stretching modes are actually pseudosymmetric and pseudoantisymmetric, but we will use the simpler terms symmetric and antisymmetric in this article.

TABLE III

PSEUDOHALOGEN INFRARED VIBRATIONS IN ORGANOMETALLIC PSEUDOHALIDES

Compound	ν_{as}	ν_{sym}	δ	ν_{M-Ps}	References
<i>Azides</i>					
$(CH_3)_3SiN_3$	2141	1332	685	528	37
$(C_2H_5)_3SiN_3$	2136	1324	679	—	3
$(C_6H_5)_3SiN_3$	2149	1308	660	—	3
$(CH_3)_3GeN_3$	2102	1290	670	456	37
$(CH_3)_2Ge(N_3)_2$	2110	1282	680	—	3
$(CH_3)_3SnN_3$	2088	1286	674	401	37
$(CH_3)_2Sn(N_3)_2$	2062	1278	660	—	3
$(CH_3)_3PbN_3$	2034	1279	655	—	37
$C_2H_5HgN_3$	2050	1280	646	—	3
$(C_6H_5)_3Sb(N_3)_2$	2081	1261	655	—	3
<i>(Iso)Cyanates</i>					
$(CH_3)_2BNCO$	2285	1505	580	1111	38
$(C_6H_5)_2BNCO$	2283	1520	625	—	39
$C_6H_5B(NCO)_2$	2257	1520	607	—	39
$(CH_3)_3SiNCO$	2290	1435	616	521	37, 40
$(CH_3)_2Si(NCO)_2$	2265	1448	630	523	40
$CH_3Si(NCO)_3$	2280	1461	623	517	40
$(CH_3)_3GeNCO$	2240	1415	606	454	37
$(CH_3)_3SnNCO$	2243	1375 ?	618	400	37
$(CH_3)_3PbNCO$	2190	1325 ?	606	—	37
<i>(Iso)Thiocyanates</i>					
$(C_6H_5)_2BNCS$	2075	891	660	—	39
$C_6H_5B(NCS)_2$	2024	849 ?	633	—	
$(CH_3)_3SiNCS$	2080	956	470	436	37, 41
$(CH_3)_2Si(NCS)_2$	2074, 2062, 2010	1015	465	433	41
$CH_3Si(NCS)_3$	2095, 2005	1050	483	—	42
$(CH_3)_3GeNCS$	2075	892	476	—	37
$(CH_3)_3SnNCS$	2073	1065, 1030, 1005	478	—	37
$(CH_3)_3PbNCS$	2090	930 ?	464	—	37
<i>(Iso)Selenocyanates</i>					
$CH_3Hg(SeCN)$	2140	540	395, 374	—	43
$C_6H_5Hg(SeCN)$	2129	542	389, 373	246	43
$(CH_3)_3Si(NCSe)$	2050	617 ?	468 ?	—	44
$(C_6H_5)_3Sn(NCSe)$	2108	—	—	—	45
$(C_6H_5)_3Pb(SeCN)$	2102	—	—	—	45

TABLE III—*continued*

Compound	ν_{as}	ν_{sym}	δ	ν_{M-PS}	Refer- ences
<i>Fulminates</i>					
C_6H_5HgCNO	2194	1200	484	314	46
$o-CH_3C_6H_4HgCNO$	2193	1209	—	—	46
$1-C_{10}H_7HgCNO$	2187	1212	486	334	46
C_6H_5HgCNO	2181, 2162	1228	493, 482	313	46
$(CH_3)_2TiCNO$	2061	1080	461	—	46
$(C_6H_5)_2TiCNO$	2042	1072	488	260	46
$(C_6H_5)_3SiCNO$	2200	1302	526	562	36
$(C_6H_5)_3GeCNO$	2164	1276	—	—	36
$(C_6H_5)_3SnCNO$	2156	1165	484	499	36
$(C_6H_5)_3PbCNO$	2123	1149	483	492	36

general the metal has only secondary influence on the pseudohalogen vibrations. However, both the symmetric and asymmetric stretching bands appear at abnormally high frequency in azides and isocyanates of silicon, and in dimethylboron isocyanate. This has been interpreted as due to $N \rightarrow$ Metal dative π bonding in these compounds (8, 13, 38, 41). The asymmetric stretching band has been the most frequently studied, because of its intensity and unusual position in the infrared. In the azides, cyanates, and fulminates of the Group IV metals, ν_{as} declines in frequency with increasing atomic number, $Si > Ge > Sn > Pb$; but little variation is observed among the isothiocyanates.

In addition to the bands discussed above, organometallic pseudohalides have metal-pseudohalogen stretching and deformation modes. The stretching mode gives infrared absorption below 600 cm^{-1} (Table III). In the few compounds which have been studied, the band appears at about the same frequency as in the analogous organometallic chloride. Metal-pseudohalogen deformation bands lie at still lower frequency and have seldom been observed. In trimethylsilyl pseudohalides, a band at 280 cm^{-1} has been assigned to one of these modes (37).

D. Ultraviolet Spectra

The azide and thiocyanate groups give rise to absorption in the accessible region of the ultraviolet. Spectral data for the compounds which have been

TABLE IV
 ULTRAVIOLET ABSORPTIONS IN ORGANOMETALLIC PSEUDOHALIDES

Compound	Frequency (cm ⁻¹)	(Wavelength, m μ)	Log ϵ	Solvent	Refer- ences
Si(NCS) ₄	40,800	(245)	3.67	CH ₂ Cl ₂	47
	34,500	(290) sh.	—	—	—
H ₃ SiNCS	40,500	(247)	1.53	Vapor	48
(CH ₃) ₃ CNCS	40,300	(248)	3.05	Dioxane	49
(CH ₃) ₃ SiNCS	42,000	(238)	2.91	CH ₃ CN	44
	35,100	(285) sh.	—	—	—
(CH ₃) ₃ GeNCS	42,000	(238)	n.a. ^a	CH ₂ Cl ₂	44
(CH ₃) ₃ SnNCS	42,000	(238)	~ 3.0	iso-C ₃ H ₇ OH	44
H ₃ SiN ₃	47,400	(211)	2.5	Vapor	50
(CH ₃) ₃ CN ₃	34,700	(288)	1.36	CH ₃ CN	13
	46,400	(216)	2.70	CH ₃ CN	—
(CH ₃) ₃ SiN ₃	39,600	(253)	1.36	CH ₃ CN	13
	47,200	(212)	2.40	—	—
(CH ₃) ₃ GeN ₃	39,500	(253)	1.32	(C ₂ H ₅) ₂ O	13
	47,400	(211)	2.39	—	—
(CH ₃) ₃ SnN ₃	43,500	(230)	2.48	iso-C ₃ H ₇ OH	13
(CH ₃) ₃ PbN ₃	42,100	(238)	3.46	iso-C ₃ H ₇ OH	13

^a n.a., not available.

studied is listed in Table IV, and spectra for some representative compounds are shown in Fig. 1. Trialkylsilyl and -germyl azides resemble alkyl azides in giving two ultraviolet absorption bands (13); the lower frequency band appears at higher energy in the silicon and germanium compounds than in organic azides. An assignment has been made by Thayer and West and the frequency shift has been rationalized in terms of ground-state stabilization by dative pi bonding. The argument is complex, and the original paper should be consulted for details (13). Trimethyltin and -lead azides give only a single band at intermediate frequency, as do the ionic alkali metal azides.

No assignment has yet been made for the ultraviolet absorption of the isothiocyanate group, but it is most likely of $n \rightarrow \pi^*$ type involving the lone pairs on sulfur. If so, the nature of the metal should have little influence on the frequency, and data in the table show that the trimethylsilicon, germanium, and tin compounds all absorb at the same energy. Covalent cyanides and cyanates do not normally absorb below 50,000 cm⁻¹ in the ultraviolet, but a band of unknown origin at 36,400 cm⁻¹ (275 m μ), has been observed for trimethyltin and trimethyllead (iso)cyanate (44).

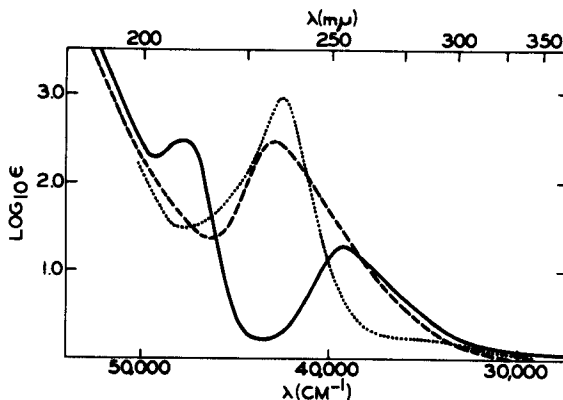


FIG. 1. Ultraviolet spectra of some organometallic pseudohalides: —, $(\text{CH}_3)_3\text{SiN}_3$; ····, $(\text{CH}_3)_3\text{SnN}_3$; ----, $(\text{CH}_3)_3\text{SiNCS}$.

IV

STRUCTURAL ISOMERISM AND CHEMICAL BONDING

All of the pseudohalogens, except for the centrosymmetric azide group, can bond through different atoms, raising the problem of which form is actually present (see Table I). Evidence on these structural questions is summarized in this section.

A. (*Iso*)Cyanides

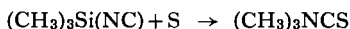
The structures of organometallic (*iso*)cyanides have long been controversial. Infrared spectroscopy unfortunately does not provide an unequivocal structural criterion for these compounds. Although the $\text{C}\equiv\text{N}$ stretching bands for organic isocyanides generally appear at slightly lower frequencies than those for nitriles (51), the ranges are too close to permit structural assignments in organometallic CN derivatives. Chemical evidence has generally been thought to favor the isocyanide structure, $\text{R}_n\text{M}-\text{N}\equiv\text{C}$. However, three of the four compounds which have been studied by X-ray crystallography have the normal cyanide structure, $\text{R}_n\text{M}-\text{C}\equiv\text{N}$ in the solid state. The molecular arrangements of these crystals are discussed below, and structural parameters are summarized in Table V.

TABLE V
X-RAY STRUCTURAL PARAMETERS FOR ORGANOMETALLIC CYANIDES

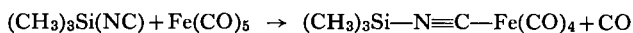
Compound	M—CH ₂ — (Å)	M—C≡ (Å)	C≡N (Å)	∠—CH ₂ —M—CN	CN → M (Å)	Refer- ences
(CH ₃) ₃ GeCN	1.98	1.98	1.15	104°	3.57	52
(CH ₃) ₃ Sn(CN)	2.16	2.49	1.09	90°	2.49	53
(CH ₃) ₂ AsCN	1.93	2.01	1.16	89°	3.18	54
CH ₃ As(CN) ₂	2.00	1.98	1.09, 1.15	93.4°, 98.6°	2.94	55

1. Organosilicon (Iso)Cyanides

Arguments have been put forward in favor of the isocyanide structure, the normal cyanide structure, and an equilibrium mixture of both forms for the important compound (CH₃)₃SiCN first prepared by McBride and Beachell (51). The original discoverers, reasoning largely from chemical evidence, favored the isocyanide structure. The reactions of (CH₃)₃Si(CN) with halogens, and especially that with sulfur to form the isothiocyanate, are analogous to those of organic isocyanides (51).



The same is true of the reaction with iron pentacarbonyl described by Seyferth and Kahlen (56).



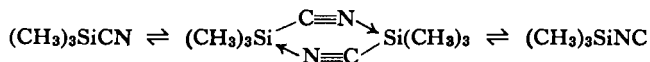
These reactions are most easily explained as being those of the isocyanide, but other interpretations are possible; for instance, the reaction with sulfur could take place by formation of the thiofulminate, followed by rearrangement,



Moreover, the reactions could take place by rearrangement of the normal cyanide with the formation of the isocyanide as a transient intermediate at the elevated reaction temperatures. Thus the chemical evidence does not permit firm conclusions about the structure of the reacting (iso)cyanides.

In 1958 Linton and Nixon studied the main C≡N stretching absorption band of (CH₃)₃Si(CN) at 2198 cm⁻¹ and showed that the positions of isotopic satellite bands were consistent with the cyanide rather than the isocyanide structure (57). However, in the same year, Bither *et al.* proposed

that $(\text{CH}_3)_3\text{Si}(\text{CN})$ was actually an equilibrium mixture containing appreciable amounts of both cyanide and isocyanide forms (29).



These workers observed that the principal CN stretching band in this compound, and also in $(\text{C}_2\text{H}_5)_3\text{Si}(\text{CN})$, was accompanied by a weaker absorption near 2100 cm^{-1} (Table IV). The weak band was attributed to the isocyanide, consistent with the fact that organic isocyanides usually give C—N absorption at lower frequency than nitriles (51). The ratio of intensities for the bands is about 5:1 at room temperature, but because isocyanides normally give $\text{C}\equiv\text{N}$ stretching bands about twice as strong as those for nitriles, the silicon compound was thought to be about a 10:1 mixture of cyanide:isocyanide. In the triethylsilyl compound the relative intensity of the 2100-cm^{-1} band increased at higher temperatures; this was interpreted as arising from the temperature dependence of the equilibrium in the equation above, favoring a larger amount of isocyanide at higher temperatures.

The "equilibrium" theory is an attractive one, but it has been called into question by Ebsworth, who points out that the 2100-cm^{-1} bands might be due to overtone or combination modes, perhaps strengthened by Fermi resonance (58). Silyl cyanide itself has been studied by microwave spectroscopy and shown to have the normal cyanide structure, $\text{H}_3\text{Si}-\text{C}\equiv\text{N}$ (58). This compound, like other silyl derivatives such as $(\text{C}_6\text{H}_5)_3\text{SiCN}$, shows only a single $\text{C}\equiv\text{N}$ band near 2200 cm^{-1} (Table IV). Allerhand and Schleyer have recently shown that $(\text{CH}_3)_3\text{Si}(\text{CN})$ behaves as a weak base toward phenol, resembling normal nitriles rather than isocyanides (59). They also noted that the proton NMR spectrum of the compound consists of a single sharp peak at 20 cps downfield from tetramethylsilane, and so provides no evidence for the isocyanide structure.

It now seems clear that $(\text{CH}_3)_3\text{Si}(\text{CN})$ and other organosilyl cyanides exist principally in the normal cyanide form, but it is not certain whether they are in equilibrium with the isocyanide, and, if so, whether this accounts for the infrared band at 2105 cm^{-1} found for some compounds. In the absence of a complete structural determination, useful information might be provided by N^{14} or C^{13} NMR spectroscopy.

2. Organogermanium and Organotin (Iso)Cyanides

The germanium compound $(\text{CH}_3)_3\text{Ge}(\text{CN})$ is a solid melting at 38°C . In solution, it has two infrared bands in the $\text{C}\equiv\text{N}$ region (Table IV), and

it also undergoes reactions with sulfur and iron carbonyl similar to those of the silicon analog. This evidence was interpreted to indicate that $(\text{CH}_3)_3\text{GeCN}$ shows an equilibrium similar to $(\text{CH}_3)_3\text{SiCN}$ (30). However, a recent single-crystal X-ray structural determination for $(\text{CH}_3)_3\text{GeCN}$ by

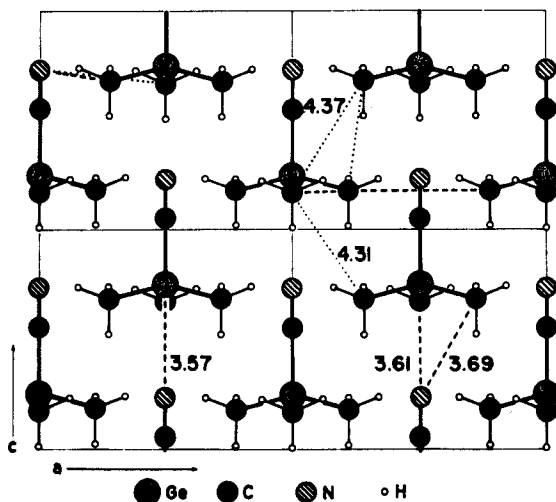


FIG. 2. Crystal structure of $(\text{CH}_3)_3\text{GeCN}$ (52). Projection on ac plane showing approximate tetrahedral coordination about Ge and lack of $\text{N} \cdots \text{Ge}$ bridging.

Schlemper and Britton shows that the solid has the normal cyanide structure, with a covalent $\text{Ge}-\text{CN}$ link and no bridging to adjacent germanium (52) (Fig. 2). However, the presence of small amounts of isocyanide co-crystallized with the cyanide could not be definitely ruled out. It is possible, of course, that isocyanide could be present in liquid and dissolved $(\text{CH}_3)_3\text{Ge}(\text{CN})$, even if absent in the solid.

Organotin (iso)cyanides give only a single infrared $\text{C}\equiv\text{N}$ band, which falls at 2175 and 2165 cm^{-1} for $(\text{CH}_3)_3\text{Sn}(\text{CN})$ and $(n\text{-C}_4\text{H}_9)_3\text{Sn}(\text{CN})$, respectively. Because the tri-*n*-butyl compound reacts with sulfur to form the isothiocyanate even at 46°C , it has been supposed to have the isocyanide structure (60), but this reaction may merely imply lability of the $\text{Sn}-\text{C}$ bond in the normal cyanide. Recently an X-ray diffraction study of crystalline trimethyltin cyanide has been carried out by Schlemper and Britton (53). This compound has a remarkable structure, in which *disordered* CN groups are symmetrically disposed on either side of the planar $(\text{CH}_3)_3\text{Sn}$ groups, to give infinite polymeric chains, with five-coordinate tin atoms (Fig. 3).

The Sn—C and Sn—N distances were equal within the experimental error, but this was large, so it is not certain that the CN groups are equally bonded at both ends. In any case, the structure in this solid is intermediate between the normal and isocyanide forms. The C—N bond distance is very short,

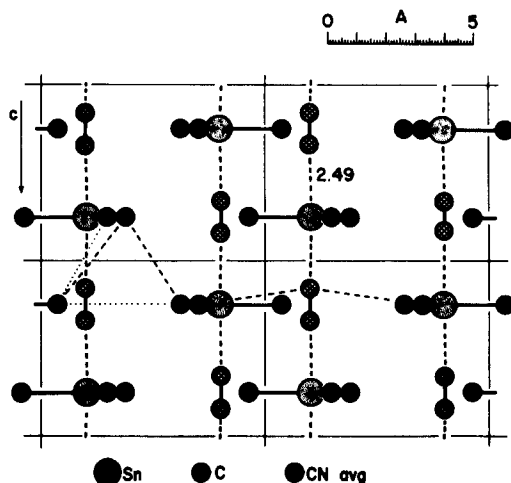


FIG. 3. Crystal structure of $(\text{CH}_3)_3\text{SnCN}$ (53). Projection showing planar arrangement of methyl groups about Sn, and Sn---CN---Sn bridging.

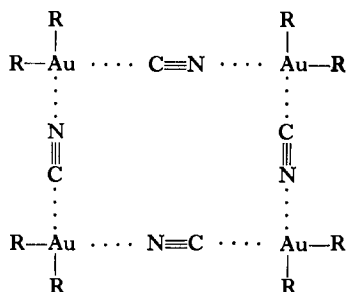
1.09 Å, indicating that the CN group is essentially ionic. The C—N bond length is 1.05 Å in sodium cyanide, but is usually about 1.16 Å in covalent cyanides (61).

The polymeric structure of $(\text{CH}_3)_3\text{Sn}(\text{CN})$ must be broken up when the compound melts or dissolves, but as yet there is no firm evidence on whether the tin remains attached to nitrogen or carbon when this happens.

3. (Iso)Cyanides of Other Metals

Both $(\text{CH}_3)_2\text{AsCN}$ (54) and $\text{CH}_3\text{As}(\text{CN})_2$ (55) have recently been shown by X-ray diffraction studies to have the $\text{As—C}\equiv\text{N}$ structure with expected As—C distances of about 2.00 Å (Table V). In these crystals, intermolecular association takes place with the CN group bridging to arsenic on a neighboring molecule. The sum of van der Waals radii for As and N, in the absence of interaction, should be 3.5 Å. The observed intermolecular N—As distance increases from 2.74 Å in $\text{As}(\text{CN})_3$ (62) to 2.94 Å in $\text{CH}_3\text{As}(\text{CN})_2$ to 3.18 Å in $(\text{CH}_3)_2\text{AsCN}$, implying that bridge bonding becomes weaker with increasing alkyl substitution.

Bridging by cyanide in an organometallic cyanide was discovered much earlier for di-*n*-propyl gold cyanide, which was investigated using X-ray crystallography by Phillips and Powell (63). The structural units are four-fold polymers with a square arrangement.



This structure permits planar four-coordination about the gold atoms. In this study carbon and nitrogen atoms could not be distinguished, but the CN groups appeared to be about equidistant between gold atoms; the Au—Au distance is 5.18 Å. Other organometallic cyanides of gold are also associated, and may have similar structures.

The same type of fourfold structure with cyanide bridging has been proposed for the dimethyl (iso)cyanides of Al, Ga, and In, which are tetrameric in benzene solution (64). Dibutylboron (iso)cyanide is even more highly associated, forming a low molecular weight polymer (65). Dimethyl-thallium cyanide, on the other hand, appears to be an ionic substance containing $(\text{CH}_3)_2\text{Tl}^+$ and CN^- ions; it is a strong 1:1 electrolyte in water (64).

B. (Iso)Cyanates

The available evidence indicates that most, if not all, organometallic NCO derivatives have the isocyanate structure with metal–nitrogen bonding. The iso structure has been established conclusively by electron diffraction for $(\text{CH}_3)_3\text{SiNCO}$ (66) and by relatively complete vibrational spectroscopic studies for $(\text{CH}_3)_2\text{B}(\text{NCO})$ (38); $\text{Si}(\text{NCO})_4$ (67); $\text{Ge}(\text{NCO})_4$ (67); and the methylsilyl isocyanates, $(\text{CH}_3)_3\text{SiNCO}$, $(\text{CH}_3)_2\text{Si}(\text{NCO})_2$, and $\text{CH}_3\text{Si}(\text{NCO})_3$ (40).

Infrared spectroscopy is an important aid in establishing the structure of

organometallic NCO compounds. Although both normal and isocyanates show asymmetric stretching bands in the same region between 2200 and 2300 cm^{-1} , the symmetric stretching frequency is quite different for these two classes of compounds. Organic isocyanates have ν_{sym} near 1400 cm^{-1} (68), whereas this band is expected to appear below 1200 cm^{-1} in normal cyanates (69). In phenyl cyanate, $\text{C}_6\text{H}_5\text{—OCN}$, it falls at 1190 cm^{-1} (69).

Those organometallic NCO compounds whose infrared spectra have been studied all show ν_{sym} near 1400 cm^{-1} , and so can be assigned the isocyanate structure with some confidence. In the methylsilyl isocyanates, this key band appears at 1435 to 1470 cm^{-1} (Table III). Other compounds showing an isocyanate symmetric stretching band include dimethylboron isocyanate (38) and the trimethyl compounds of germanium and (probably) tin and lead (37). A number of other organoboron derivatives have also been assigned the isocyanate structure on the basis of infrared data (39, 70). Sometimes, as in the case of more complex triorganotin (iso)cyanate compounds, the symmetric stretching band cannot be identified with certainty and the iso structure can only be inferred (28).

It is somewhat surprising that no organometallic cyanates with M—OCN bonding have been reported, even for elements like silicon which normally form more energetic bonds to oxygen than to nitrogen. Apparently the tendency of NCO to bond at nitrogen rather than oxygen is quite strong; organic cyanates are difficult to prepare and are unstable with respect to decomposition to the isocyanate (69, 71). Organometallic cyanates with M—O bonding may possibly be prepared at sufficiently low temperatures.

C. (Iso)Thiocyanates and (Iso)Selenocyanates

For these compounds the evidence is less firm than for isocyanates, and is limited to derivative of Group IV elements and boron. However, the compounds which have been studied all appear to have the isothiocyanate structure, $\text{R}_n\text{M—NCS}$. The iso structure has been established for $(\text{CH}_3)_3\text{SiNCS}$ by electron diffraction (66) and for H_3SiNCS by microwave spectroscopy (72, 72a, 73). Several NCS compounds were assigned the iso structure on the basis of their molecular refraction by Anderson at an early date (74). This method has occasionally been used since, but its reliability is doubtful, and most of the recent studies have based structural assignments on infrared and/or Raman spectroscopy.

As for NCO compounds, the asymmetric stretching vibrations of both normal and iso thiocyanates lie at almost the same frequency, near 2100 cm^{-1} (75). Reliable structural assignments for organometallic (iso)thiocyanates therefore cannot be made using the frequency of this mode. The NCS symmetric stretching band offers more promise, for this falls at distinctly higher frequency in isothiocyanates than in thiocyanates. Previously there was some controversy in the literature concerning the position of ν_{sym} , but it now seems to be firmly established that this band appears between 950 and 1100 cm^{-1} in organic isothiocyanates (76) and near 700 cm^{-1} in thiocyanates. The frequencies are 1088 cm^{-1} and 680 cm^{-1} for CH_3NCS and CH_3SCN , respectively (76, 77). The symmetric stretching frequency is rather dependent on the nature of the substituent. This frequency has been used to decide between $\text{M}-\text{NCS}$ and $\text{M}-\text{SCN}$ bonding in transition metal complexes; bonding to nitrogen (the iso structure) gives ν_{sym} at $780\text{--}860\text{ cm}^{-1}$ compared to $690\text{--}720\text{ cm}^{-1}$ for sulfur-metal bonding (78).

Raman and infrared spectroscopic studies have been carried out for two methylsilyl NCS derivatives, both of which appear to have the isothiocyanate structure (41); ν_{sym} falls between 950 and 1050 cm^{-1} for these compounds, increasing with the number of NCS groups (Table III). Carlson has carried out a complete vibrational analysis of $\text{Si}(\text{NCS})_4$ (47), which shows ν_{sym} at 1087 cm^{-1} . A variety of covalent inorganic NCS derivatives have also been found to have ν_{sym} in the 1000-cm^{-1} region (42, 79), and are probably also isothiocyanates. Recently a number of dialkyltin NCS compounds have been described, all having a band at $820\text{--}850\text{ cm}^{-1}$ attributed to the symmetric stretch. On this basis these compounds were assigned the iso structure (80, 81). A large number of boron compounds, mostly inorganic derivatives, have also been shown to have the isothiocyanate arrangement (39).

A somewhat different approach towards structural determination of NCS derivatives has recently been employed by Cummins and Dunn, who point out that organic isothiocyanates normally have an asymmetric stretching absorption about fifty times more intense than that of organic thiocyanates. The absorbance of ν_{as} for tri-*n*-butyltin isothiocyanate (at 2032 cm^{-1}) was found to be roughly equal to that for organic isothiocyanates, and so the iso structure was assigned (60).

No evidence is available concerning the structure of organometallic NCS derivatives of Hg, Tl, As, Sb, and Bi, and some of these elements normally bond preferentially to sulfur rather than to nitrogen. In determining

structures of organometallic (iso)thiocyanates, N^{14} NMR spectroscopy could be highly useful. It has recently been shown that this method can be used to distinguish iso or normal structure in both organic SCN compounds and metal complexes containing SCN ligands (82).

(Iso)selenocyanates have been studied the least of all the pseudohalides. Organic compounds have both "normal" and "iso" forms (45, 83–86), and, unlike the corresponding O and S compounds, organic selenocyanates do *not* convert to the "iso" compounds upon heating (83). $C_6H_5Hg(SeCN)$, $CH_3Hg(SeCN)$, and $(C_6H_5)_3Pb(SeCN)$ (43, 45) are interpreted as having the "normal" form on the basis of their ν_{as} being a single, sharp peak about 2100 cm^{-1} ; on the other hand, $(C_6H_5)_3Sn(NCSe)$ (45) and $(CH_3)_3Si(NCSe)$ (44) have broad peaks at 2108 and 2050 cm^{-1} , with satellite peaks at 2144 and 2080 cm^{-1} , respectively, and so may have the iso structure. Organic isoselenocyanates have a very strong, broad peak about 2110 cm^{-1} , usually with satellites at higher (or lower) frequencies, while organic selenocyanates have a weaker, sharp peak about $2150\text{--}2160\text{ cm}^{-1}$ (83, 84, 86). Assignments, however, are still quite uncertain.

D. Fulminates

There are no known isofulminates, all organic derivatives having the nitrile oxide structure, $R-CNO$. The fact that organometallic CNO derivatives give ν_{sym} at higher frequency than fulminate ion (36) indicates that they too have the carbon-bonded structure, for $R_nM-O-N\equiv C$ compounds would be expected to have a very low frequency for ν_{O-N} (ν_{sym}). A highly ionic structure is inferred for the explosive compound $(CH_3)_2Tl^+CNO^-$ from the fact that its fulminate infrared absorption bands are very near those of the free fulminate ion (46).

E. Bonding in Derivatives of Triatomic Pseudohalides

Central to the topic of bonding in these compounds is the question of possible metal–pseudohalide pi interaction and its effect on the molecular structure. Structural information is presently available only for a few inorganic derivatives of silicon and germanium. However, detailed structures for organometallic derivatives of three-atom pseudohalides will

probably become known soon, and should be highly significant in connection with the bonding problem.

Bonding in covalent pseudohalides generally is not likely to be well understood until accurate molecular orbital calculations can be carried out. In the absence of such calculations, we will use valence-bond models to discuss qualitatively the bonding in these compounds. Linnett has previously outlined a brief valence-bond treatment of a limited number of

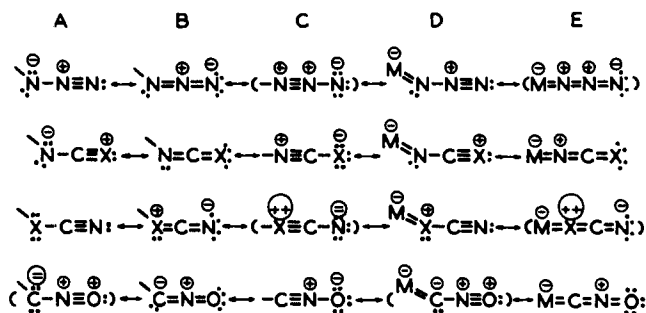


FIG. 4. Canonical structures contributing to resonance hybrid for pseudohalides. $X = O, S, \text{ or } Se$. Forms A, B, and C are for covalent pseudohalides generally, whereas forms D and E represent metal derivatives with pi bonding from pseudohalogen to metal. Unimportant contributing structures in parentheses.

covalent pseudohalides, reaching conclusions similar to ours (87). However, his approach employed the double-quartet notation, which will not be used below.

Canonical structures for covalent pseudohalides are shown in Fig. 4. For each pseudohalogen, forms A, B, and C apply to covalent derivatives generally, whereas D and E represent derivatives in which pi bonding is taking place from the pseudohalogen to the attached metal atom. Considering for the moment only A, B, and C, it can be seen that all three are reasonable contributors to the resonance hybrid for covalent isocyanates, isothiocyanates, and isoselenocyanates. However, form A for fulminates, and form C for azides, cyanates, thiocyanates, and selenocyanates violate the Pauling adjacent charge rule and so cannot be important contributors.

The preferred bond angles between the linear pseudohalide group and the attached atom are $109^\circ 28'$, 120° , and 180° for forms A, B, and C, respectively. Because form C cannot contribute, the bond angle in covalent azides should be between 109° and 120° . For isocyanates and isothiocyanates, all three forms can contribute, but electronegativities should

favor C over A. Bond angles greater than 120° are therefore expected. Data for the hydrogen and methyl derivatives are consistent with these explanations (Table VI).

TABLE VI
BOND ANGLES IN DERIVATIVES OF TRIATOMIC PSEUDOHALOGENS^a

R	Azide $\angle \text{R}-\text{N}-\text{N}$	Isocyanate $\angle \text{R}-\text{N}-\text{C}$	Isothiocyanate $\angle \text{R}-\text{N}-\text{C}$
H-	111°	128°	130°
CH ₃ -	$120^\circ \pm 5^\circ$	$125^\circ \pm 5^\circ$	142°
(CH ₃) ₃ Si-	Bent ^b	$150^\circ \pm 3^\circ$ ^c	$154^\circ \pm 2^\circ$ ^c
H ₃ Si-	Bent ^d	—	180° ^e

^a Data from Wells (61), except where noted.

^d Ebsworth and Mays (50).

^b Thayer and West (13).

^e Jenkins *et al.* (73).

^c Kimura *et al.* (66).

Significant dative pi bonding, represented by the contribution of forms D and E to the resonance hybrid, should increase the bond angle. Microwave studies have shown that in H₃SiNCS (73), the silicon atom is *collinear* with the NCX group (Table VI). Si(NCS)₄ and Si(NCO)₄ also appear from vibrational spectroscopic studies to have 180° bond angles between silicon and the attached pseudohalide groups (47, 67). The linear Si—N—C—X structure in these compounds has frequently been cited as a decisive item of evidence for dative pi bonding from N to Si in such compounds.

However, even in the absence of any special interactions, the Si—N—C bond angles are expected to be about 140° . Furthermore, the electron-releasing inductive effect of the silyl substituent alone should increase the contribution of form C at the expense of A (Fig. 4), and so increase the bond angle compared to that in alkyl derivatives. In the absence of information about other compounds, it is difficult to know to what extent the 180° Si—N—C bond angle results from increased ionicity, rather than dative pi bonding. It is therefore particularly significant that Ge(NCO)₄ (67) and H₃GeNCO (88) both appear to have *nonlinear* Ge—N—C—O arrangements. The inductive effect of Ge and Si should be nearly the same, and so the increase in the Si—N—C over the Ge—N—C bond angles (which are not yet known) is probably due to greater pi bonding in the Si than in the Ge compounds.

A recent electron-diffraction study shows that the linear arrangement in the H_3SiNCX and $\text{Si}(\text{NCX})_4$ compounds is not general for organosilicon pseudohalides; both $(\text{CH}_3)_3\text{SiNCO}$ and $(\text{CH}_3)_3\text{SiNCS}$ have angular structures, with $\text{Si}-\text{N}-\text{C}$ bond angles of 150° and 153° , respectively (66). These bond angles are somewhat larger than those in the methyl or hydrogen derivatives of the same pseudohalogens (Table VI). The $\text{N}-\text{C}$ distances both in $(\text{CH}_3)_3\text{SiNCO}$ and $(\text{CH}_3)_3\text{SiNCS}$ are only 1.18 Å, compared with 1.22 Å for the corresponding CH_3 compounds. This suggests considerable contribution from resonance form C in the silicon compounds. A nonlinear arrangement has also been proposed for $(\text{CH}_3)_3\text{SnNCS}$ on the basis of infrared spectral evidence (89).

Silyl azide (50) and trimethylsilyl azide (13) are both reported to have a nonlinear $\text{Si}-\text{N}-\text{N}$ structure, the bond angles again being unknown. As yet no conclusion can be drawn about the relative importance of dative pi bonding in silyl azides compared to the $-\text{NCO}$ and $-\text{NCS}$ derivatives. Even strong pi bonding interaction between N and Si would not necessarily lead to linear structure in azides. From Fig. 4 it is apparent that the dative pi-bonded form E, with preferred linear arrangement, can be an important contributor for isocyanate and isothiocyanate, but not for azide. However, D may be an important contributor in organometallic azides; the preferred bond angle is only 120° for this form.

These concepts can be extended to pseudohalide groups for which no structural information is yet available. Covalent cyanate and thiocyanate compounds resemble azides in that forms C and E (Fig. 4) are unimportant contributors to the resonance hybrid. It can be predicted that *covalent cyanates and thiocyanates will have bond angles less than 120°* . Organometallic cyanates and thiocyanates are predicted to have bent structures, even if there is dative pi bonding to the attached metal atom.

Fulminates represent the other extreme case. Form A cannot be an important contributor to the resonance hybrid in fulminates, and electronegativities favor form C somewhat over form B. We can therefore predict that *covalent fulminates will have bond angles decidedly larger than 120°* , probably as large or larger than the corresponding $-\text{NCO}$ and $-\text{NCS}$ compounds. In organometallic fulminates, form D cannot be a significant contributor. These compounds, particularly of metalloids like B, Si, and Ge, are quite likely to have linear structures.

Bond angles in covalent pseudohalides are probably governed by a delicate balance of many factors. If so, in favorable cases even a relatively weak dative

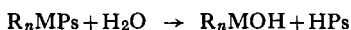
π interaction might greatly increase the bond angle. In the silyl compounds which have linear structures, a small amount of π -orbital overlap might have just such a drastic effect. Thus one should not infer that $N \rightarrow Si$ π bonding is necessarily strong; "a little bit may go a long way." Finally, it should be noted that for a given pseudohalogen, different organometallic compounds, even of the same metal, may be found to have significantly different structures. Structural data for a variety of organometallic pseudohalides is urgently needed for further progress in this area.

V

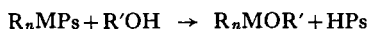
CHEMICAL PROPERTIES

A. Solvolyses

Organometallic pseudohalides, like the corresponding halides, react with water.



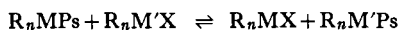
This reaction goes irreversibly to the right for derivatives of metalloids such as B or Si. True equilibrium can be established for compounds of more electropositive elements. While there have been no kinetic studies on the rates of these hydrolyses, they appear to be less than for the corresponding chlorides or bromides. Reaction with other active hydrogen compounds usually leads to solvolysis. Thus alcohols generally convert organometallic pseudohalides to alkoxides.



However, addition of protonic reagents can also take place: see Section V, E.

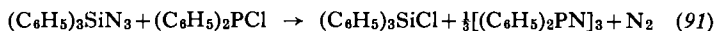
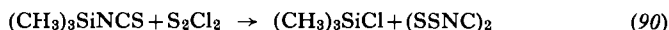
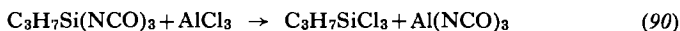
B. Exchange Reactions and the Conversion Series

The metal-pseudohalogen bond, although thermodynamically stable, is generally quite labile with respect to exchange reactions with another negative group such as a halide ion. The equilibrium



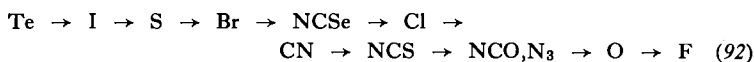
can be forced to one side or the other by appropriate conditions. The compound $R_nM'X$ need not also be an organometallic; a covalent inorganic

halide works just as well. One example is the reaction with silver pseudohalides; others are given as follows:

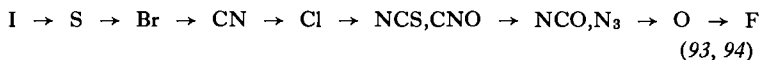


By reaction with the appropriate silver salt, a compound may be converted into one following it, but not into one preceding it, in the conversion series written

Silyl compounds, $\text{H}_3\text{Si}-$



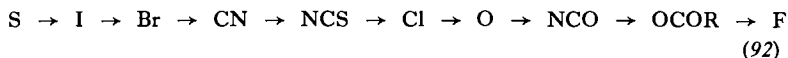
Trimethylsilyl compounds, $(\text{CH}_3)_3\text{Si}-$



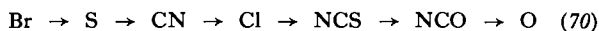
Germanium series, $\text{R}_3\text{Ge}-$



Triethyltin series, $(\text{C}_2\text{H}_5)_3\text{Sn}-$



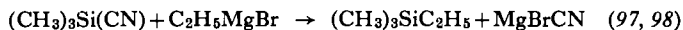
Boron series, $\text{R}_2\text{B}-$



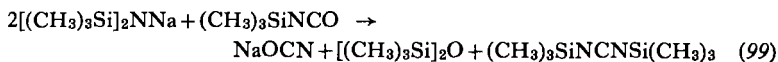
Some additions have been made since the original series were proposed in the references given above; these have been incorporated, and represent the series as they are presently known. Ebsworth has determined the positions of H_3SiN_3 (50) and H_3SiNCSe (96) in the silyl series, while Thayer and West have determined the position of $(\text{CH}_3)_3\text{SiN}_3$ (13) and Beck and Schuierer have indicated the position of $(\text{CH}_3)_3\text{SiCNO}$ (36).

C. Other Displacement Reactions

Organometallic pseudohalides are expected to react with other nucleophilic reagents to undergo displacement of the pseudohalide ion. An example is the reaction of organosilyl (iso)cyanides with Grignard reagents.



An especially interesting example is the reaction of trimethylsilyl (iso)cyanate with *N*-sodiohexamethyldisilazane to give a disilylcarbodiimide.



D. Donor—Acceptor Complexes

The pseudohalide groups of organometallic pseudohalides have lone pairs of electrons available for donor-acceptor complex formation. If the metal atom of an organometallic pseudohalide is electron-deficient, the compound can also serve as a Lewis acid; it can then form complexes with different Lewis basis, or with other molecules of the same kind to give autoassociation (polymerization). Examples are known for all three types of complexes.

1. Complexes with Other Lewis Acids

Adducts of this category have been isolated to date only for cyanides and azides. Known complexes are listed in Table VII. Halide-pseudohalide exchange reactions probably proceed through unstable intermediates of this type; such intermediates have been suggested by Wiberg (104) and Kratzer (91). For cyanides, isomerization to the more basic isocyanides may occur upon complex formation; in particular, this has been suggested for adducts of Group IV metal (iso)cyanides with iron carbonyl, which resemble other isocyanide-carbonyl complexes (30). However, no unequivocal evidence is available as to the arrangement in any cyanide complex. The $\text{C}\equiv\text{N}$ infrared band of the free (iso)cyanide shifts to lower frequency in the $\text{Fe}(\text{CO})_4$ complexes (56), but to *higher* frequency in the boron halide adducts.

Azide complexes with Lewis acids have been reported only for Group IV metals. The bonding in these adducts is presently also an unsolved structural problem, since bonding could occur either at the nitrogen attached to the metal (α complexing) or through the terminal nitrogen (γ complexing). The canonical structures shown above would indicate that α complexing

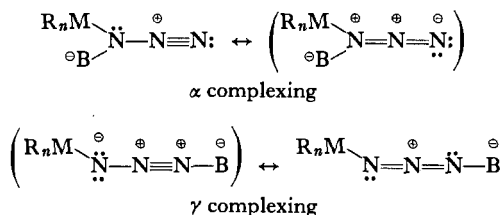


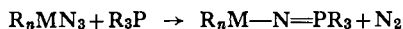
TABLE VII
 PSEUDOHALIDE ADDUCTS WITH LEWIS ACIDS

Compound	M.p. ^a (°C)	ν_{as}	References
$2(\text{C}_2\text{H}_5)_2\text{AuCN} \cdot \text{AuCN}$	dec 110°–120°	—	100
$2(\pi\text{C}_3\text{H}_7)_2\text{AuCN} \cdot \text{AuCN}$	sol	—	101
$(\text{CH}_3)_3\text{SiCN} \cdot \text{BH}_3$	sol	—	101
$(\text{CH}_3)_3\text{SiCN} \cdot \text{BF}_3$	dec -78°	—	102
$(\text{CH}_3)_3\text{SiCN} \cdot \text{BCl}_3$	dec 50°–55°	—	102
$(\text{CH}_3)_3\text{SiCN} \cdot \text{BBr}_3$	dec 25°	—	102
$(\text{CH}_3)_3\text{GeCN} \cdot \text{BF}_3$	85°–87°	2270, 2236	30
$(\text{CH}_3)_3\text{SiNC} \cdot \text{Fe}(\text{CO})_4$	47°–48°	2186	56
$(\text{CH}_3)_3\text{GeNC} \cdot \text{Fe}(\text{CO})_4$	69°–70°	2135	56
$(\text{CH}_3)_3\text{SnNC} \cdot \text{Fe}(\text{CO})_4$	subl 110°–115°/0.2	2142	56
$(\text{C}_6\text{H}_5)_3\text{SiN}_3 \cdot \text{BBr}_3$	sol	2208	103
$(\text{C}_6\text{H}_5)_3\text{GeN}_3 \cdot \text{BBr}_3$	sol	2208	103
$(\text{CH}_3)_3\text{SiN}_3 \cdot \text{BBr}_3$	sol	2208	103
$(\text{C}_6\text{H}_5)_2\text{CH}_3\text{SiN}_3 \cdot \text{BBr}_3$	liq	2210	103
$(\text{C}_6\text{H}_5)_3\text{GeN}_3 \cdot \text{SnCl}_4$	sol	2131	103
$(\text{C}_6\text{H}_5)_3\text{SnN}_3 \cdot \text{SnCl}_4$	sol	2208	103
$(\text{CH}_3)_3\text{SiN}_3 \cdot \text{SnCl}_4$	sol	2110	103
$(\text{CH}_3)_3\text{SiN}_3 \cdot \text{SbCl}_5$	sol	2210	103
$(\text{C}_6\text{H}_5)_3\text{SiN}_3 \cdot \text{P}(\text{C}_6\text{H}_5)_3$	dec 30°	2018	8, 103

^a dec T°, decomposes at T° without melting; sol, solid at room temperature; liq, liquid at room temperature; subl, sublimes.

should increase the contribution of the $\text{R}_n\text{M}-\text{N}^--\text{N}^+\equiv\text{N}$ form, strengthening the bond between the two terminal nitrogens at the expense of the other N—N bond, while γ complexing would have the opposite effect. Infrared studies show that ν_{as} shifts to higher frequency while ν_{sym} shifts to lower frequency in azide complexes compared to the free azide, suggesting α complexing (103); however, the evidence is still incomplete.

Some azide complexes dissociate at higher temperatures and recombine when cooled; $(\text{CH}_3)_3\text{SiN}_3 \cdot \text{BBr}_3$, a solid, can be distilled in this manner (103). Other complexes are highly unstable even below room temperature, undergoing rapid exchange. Like organic azides, some organometallic azides will react with phosphines to split out a molecule of nitrogen, forming a phosphineimine (3).



2. Complexes with Other Lewis Bases

Complex formation of this type requires the presence of a metal atom which can serve as a Lewis acid. Such adducts have been reported only for

TABLE VIII
PSEUDOHALIDE ADDUCTS WITH LEWIS BASES

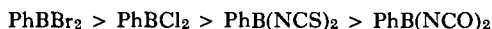
Compound	M.p. ^a (°C)	References
CH ₃ BeCN · M(CH ₃) ₃	sol	64
Na ⁺ C ₆ H ₅ B(CN) ₃ ⁻	sol	105
Na ⁺ [(<i>p</i> -FC ₆ H ₄) ₃ BCN] ⁻	sol	105a
Na ⁺ [(<i>p</i> -ClC ₆ H ₄) ₃ BCN] ⁻	sol	105a
Na ⁺ [(<i>p</i> -BrC ₆ H ₄) ₃ BCN] ⁻	sol	105a
(<i>n</i> -C ₄ H ₉) ₂ BCN · NH ₃	liq	65
(iso-C ₄ H ₉) ₂ BCN · H ₂ NC ₆ H ₅	96°–97°	16
(<i>n</i> -C ₄ H ₉) ₂ BCN · H ₂ NC ₆ H ₅	111°–112°	16
(iso-C ₄ H ₉) ₂ BCN · H ₂ NC ₄ H ₉	117°–117.5°	16
(iso-C ₅ H ₁₁) ₂ BCN · H ₂ NC ₆ H ₅	115°–115.5°	16
2(CH ₃) ₂ AlCN · C ₄ H ₈ O	sol	105b
K ⁺ C ₆ H ₅ Tl(CN) ₃ ⁻	265.5° dec	24
2(C ₂ H ₅) ₂ AuCN · H ₂ NC ₂ H ₄ NH ₂	96°–98° dec	100
2(<i>n</i> -C ₃ H ₇) ₂ AuCN · H ₂ NC ₂ H ₄ NH ₂	84°–85° dec	100
(C ₆ H ₅) ₂ BN ₃ · C ₅ H ₅ N	sol	106
(C ₃ H ₇) ₂ BN ₃ · C ₅ H ₅ N	s.b. 89°–92°/high vacuum	106
C ₆ H ₅ B(N ₃) ₂ · C ₅ H ₅ N	—	106
(C ₂ H ₅) ₂ AlN ₃ · C ₄ H ₈ O	liq	107
(CH ₃) ₃ SnN ₃ · N(C ₂ H ₅) ₃	125°–128°	37
(CH ₃) ₃ SnN ₃ · NC ₅ H ₅	136°–137°	37
C ₆ H ₅ B(NCS) ₂ · C ₅ H ₅ N	153°–155°	108
C ₆ H ₅ B(NCS) ₂ · CH ₃ CO ₂ C ₂ H ₅	46°–48°	108
(C ₂ H ₅) ₄ N ⁺ CH ₃ Sn(NCS) ₅ ²⁻	120°–121° dec	109
(C ₂ H ₅) ₄ N ⁺ (CH ₃) ₂ Sn(NCS) ₄ ²⁻	113°–115°	109
(C ₂ H ₅) ₄ N ⁺ (CH ₃) ₃ Sn(NCS) ₂	163°–169° dec	109
(C ₂ H ₅) ₂ AuSCN · (NH ₂) ₂ C=S	88°	110
(C ₂ H ₅) ₂ AuSCN · CH ₃ C(:S)NH ₂	sol	110
(CH ₃) ₂ Sn(NCS) ₂ · bipy	219°–220.5°	80
(C ₂ H ₅) ₂ Sn(NCS) ₂ · bipy	220°–222°	80
(<i>n</i> -C ₃ H ₇) ₂ Sn(NCS) ₂ · bipy	158°–159°	80
(<i>n</i> -C ₄ H ₉) ₂ Sn(NCS) ₂ · bipy	150°–150.5°	80
C ₆ H ₅ B(Cl)NCO · C ₅ H ₅ N	sol	108
C ₆ H ₅ B(NCO) ₂ · C ₅ H ₅ N	143°–145°	108
C ₆ H ₅ B(NCO) ₂ · CH ₃ CO ₂ C ₂ H ₅	Dissociates 20°/15 mm	108
2(C ₆ H ₅) ₂ Sn(NCO) ₂ · bipy	204°–206° dec	28

^a sol, solid at room temperature; liq, liquid at room temperature; T° dec, melts at T° without decomposition; b, boils at T°.

derivatives of B, Al, Sn, Au, and Tl. Known examples are listed in Table VIII. Some are covalent donor-acceptor complexes, while others are anionic, e.g. $\text{Na}^+\text{PhB}(\text{CH}_3)_3^- (\text{C}_2\text{H}_5)_4\text{N}^+(\text{CH}_3)_3\text{Sn}(\text{NCS})_2^-$

Infrared spectral studies on organotin isothiocyanate complexes have recently been carried out by Okawara and his co-workers (89). Although $(\text{CH}_3)_3\text{SnNCS}$ shows two bands attributed to NCS bending vibrations, only a single such band is found in $(\text{CH}_3)_3\text{SnNCS} \cdot \text{pyridine}$. These results are interpreted in terms of a $\text{Sn}-\text{N}-\text{C}$ arrangement in $(\text{CH}_3)_3\text{SnNCS}$ and a linear structure for the pyridine complex. Infrared spectral features also suggest *cis* coordination of NCS groups in $(\text{CH}_3)_2\text{SnNCS} \cdot \text{bipyridine}$, and a *trans* octahedral arrangement in $(\text{CH}_3)_2\text{Sn}(\text{NCS})_4^-$ (89).

The heats of formation of addition complexes of pyridine and ethyl acetate with phenylhalo- and phenylpseudohaloboranes have been the subject of a recent study by Lappert and Pyszora, who found the following order of acceptor strengths (70):



The weaker acid strength of the pseudohalides compared to the chloride and bromide may result from $\text{N}-\text{B}$ pi bonding, which should lower the acidity of boron.

3. Polymers

Intermolecular association of organometallic pseudohalides can take place through donor-acceptor bonding from the lone pairs of pseudohalogens to unfilled metal orbitals. Polymerized organometallic pseudohalides are listed in Table IX. It is this sort of association which takes place in the polymeric cyanides whose structures were discussed in Section III, B. Polymerization is particularly well established for organometallic (iso)-cyanides, which polymerize either to form tetramers or high polymers.

Isocyanates of boron are initially formed as monomers, but polymerize slowly on standing (39). However, it is not yet certain whether this association involves the boron atom. Polymerization through the isocyanate group itself could take place, as it does for organic isocyanates, though much less readily.

Methyltin pseudohalides generally are solids with melting points much higher than the corresponding halides, indicating that they are associated, probably with considerable ionic character in the Sn -pseudohalide bonds. This has been shown by the X-ray structural study of $(\text{CH}_3)_3\text{SnCN}$ (Section B, 2) and is also suggested by the infrared spectra of $(\text{CH}_3)_3\text{SnN}_3$

(13, 37, 113, 114) and $(\text{CH}_3)_3\text{Sn}(\text{NCO})$ (37). Organogold and organo-aluminum pseudohalides, insofar as they have been studied, also show a strong tendency toward polymerization, reflecting the high electron deficiency of these metals.

TABLE IX
POLYMERIZED ORGANOMETALLIC PSEUDOHALIDES

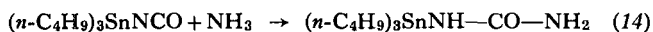
Compound	Degree of polymerization	References
$(n\text{-C}_4\text{H}_9)_2\text{BCN}$	Polymer	65
$(\text{CH}_3)_2\text{AlCN}$	Tetramer, octamer	64, 105b
$(\text{C}_2\text{H}_5)_2\text{AlCN}$	Heptamer	105b
$(\text{CH}_3)_2\text{GaCN}$	Tetramer	64
$(\text{CH}_3)_2\text{InCN}$	Tetramer	64
$(\text{CH}_3)_3\text{SnCN}$	Polymer	52
$(\text{CH}_3)_2\text{Sn}(\text{CN})_2$	Polymer	111
$(\text{CH}_3)_2\text{AsCN}$	Polymer	54
$\text{CH}_3\text{As}(\text{CN})_2$	Polymer	55
$(\text{CH}_3)_3\text{PtCN}$	Polymer	112
$(\text{C}_2\text{H}_5)_2\text{AuCN}$	Tetramer	100
$(n\text{-C}_3\text{H}_7)_2\text{AuCN}$	Tetramer	100
$(\text{CH}_3)_2\text{BNCO}$	Polymer	38
$(\text{C}_6\text{H}_5)_2\text{BNCO}$	Polymer	39
$\text{C}_6\text{H}_5\text{B}(\text{NCO})_2$	Polymer	39
$(\text{CH}_3)_3\text{SnNCO}$	Polymer	37
$(\text{CH}_3)_2\text{Sn}(\text{NCO})_2$	Polymer	11
$(\text{C}_2\text{H}_5)_2\text{AlN}_3$	Dimer	20a, 107
$(\text{CH}_3)_3\text{SnN}_3$	Polymer	13, 37, 113
$(\text{CH}_3)_2\text{Sn}(\text{N}_3)_2$	Polymer	11
$(\text{CH}_3)_3\text{SnNCS}$	Polymer	37
$(\text{CH}_3)_2\text{Sn}(\text{NCS})_2$	Polymer	11
$(\text{C}_2\text{H}_5)_2\text{AuSCN}$	Dimer	110

E. Additions to the Pseudohalide Group

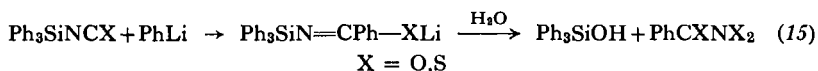
Organic cyanides, isocyanates, and isothiocyanates ordinarily react with protonic materials to give addition across the multiple bonds of the pseudohalogen. Such addition reactions are the exception for organometallic pseudohalides, which are usually solvolyzed by protonic reagents (Section IV, A). However, organosilicon isocyanates react with amines to give silyl ureas.



Tri-*n*-butyltin isocyanate is also reported to add ammonia, amines, and alcohols in a manner analogous to organic isocyanates.

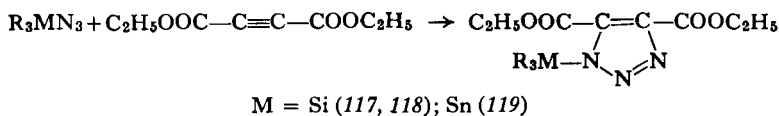


Triphenylsilyl isocyanate and isothiocyanate have also been postulated to add phenyllithium across the C—X double bond.



The hydrogenolysis of $(\text{CH}_3)_3\text{Si}(\text{CN})$ with Raney nickel catalyst to give hexamethyldisilazane is also thought to proceed by addition to the $\text{—C}\equiv\text{N}$ bond (51, 116).

Organometallic azides of the Group IV elements will add to acetylenes to give triazoles.



VI

TABLES OF PROPERTIES

Tables X–XV summarize properties of the known organometallic pseudohalides of nontransition elements. Methods of preparation given in the Tables refer to the subsection headings in Section II. Within the tables, for each metal, compounds are ordered according to the number of pseudohalogen groups, and, if these are equal, by increasing complexity of the organic groups.

TABLE X
ORGANOMETALLIC (ISO)CYANIDES

Compound	Synthetic method ^a	M.p. ^b (°C)	B.p. ^b (°C)/mm	References
<i>Beryllium</i>				
CH ₃ BeCN	B3	sol	—	64
<i>Zinc</i>				
CH ₃ ZnCN	A2	sol	—	119a
<i>Mercury</i>				
CH ₃ HgCN	A2	93°	—	120, 121
C ₂ H ₅ HgCN	A2	77°	—	122
<i>n</i> -C ₃ H ₇ HgCN	A2	28°	—	122
<i>n</i> -C ₄ H ₉ HgCN	A2	42°	—	122
C ₅ H ₅ HgCN	—	—	—	123
<i>n</i> -C ₅ H ₁₁ HgCN	A2	39°	—	122
C ₆ H ₅ HgCN	B5	204°–205°	—	124
cyclo-C ₆ H ₁₁ HgCN	B5	144°	—	124
<i>n</i> -C ₆ H ₁₃ HgCN	A2	38°	—	122
C ₆ H ₅ CH ₂ HgCN	B5	124°	—	124
<i>p</i> -CH ₃ OC ₆ H ₄ HgCN	A2	167.5°	—	125
<i>n</i> -C ₇ H ₁₅ HgCN	A2	53°	—	122
<i>Boron</i>				
(<i>n</i> -C ₄ H ₉) ₂ BCN	A2, B5	oil	—	65
(<i>iso</i> -C ₄ H ₉) ₂ BCN	B3	145°	—	16
(<i>iso</i> -C ₅ H ₁₁) ₂ BCN	B3	oil	—	16

TABLE X—*continued*

Compound	Synthetic method ^a	M.p. ^b (°C)	B.p. ^b (°C)/mm	References
<i>Aluminum</i>				
(CH ₃) ₂ AlCN	B3	89°	—	64, 105b
(C ₂ H ₅) ₂ AlCN	A1	l.	—	105b
<i>Gallium</i>				
(CH ₃) ₂ GaCN	B3	79°	—	64
<i>Indium</i>				
(CH ₃) ₂ InCN	B3	147°	—	64
<i>Thallium</i>				
(CH ₃) ₂ TlCN	A1, A2, B3	275° dec	—	64, 126, 126a
(C ₂ H ₅) ₂ TlCN	A3	sol	—	127
(C ₆ H ₅) ₂ TlCN	A1	318° dec	—	24
C ₆ H ₅ Tl(CN) ₂	B1	228° dec	—	24
<i>Silicon</i>				
(CH ₃) ₃ SiCN ^c	A2, B3	11.5°	117.8°	93
(C ₂ H ₅) ₃ SiCN ^d	A2	5.5°	182°	29, 93
(<i>n</i> -C ₃ H ₇) ₃ SiCN	A2	—8°	229°	93
(C ₆ H ₅) ₃ SiCN	A2, B5	135°–137°	—	29
(CH ₃) ₂ Si(C ₆ H ₅)CN ^e	A2	—	230°–232°	128
CH ₃ SiH ₂ CN	A2	23.1°	0°/26.5	129
(CH ₃) ₂ SiHCN	A2	—60.9°	0°/11.5	130
C ₇ H ₁₅ SiH ₂ CN ^f	A2	—	204°	10
(CH ₃) ₅ Si ₂ CN ^g	A2	25°	85°–87°/34	27

$(\text{CH}_3)_7\text{Si}_3\text{CN}$	C1	—	$36^\circ\text{--}40^\circ/0.4$	27
$(\text{CH}_3)_{10}\text{Si}_4\text{CN}$	C1	—	$65^\circ\text{--}67^\circ/0.4$	27
$(\text{CH}_3)_{13}\text{Si}_5\text{CN}$	C1	—	$67.5^\circ\text{--}71^\circ/0.2$	27
$(\text{CH}_3)_{16}\text{Si}_6\text{CN}$	C1	—	—	27
$(\text{C}_2\text{H}_5)_2\text{Si}(\text{CN})_2$	A2	33°	214°	131
$(\text{CH}_3)_4\text{Si}_2(\text{CN})_2$	A2	—	—	27
$(\text{CH}_3)_{16}\text{Si}_8(\text{CN})_2$	C1	—	—	27
<i>Germanium</i>				
$(\text{CH}_3)_3\text{GeCN}$	A2	$38^\circ\text{--}38.5^\circ$	—	30
$(\text{C}_2\text{H}_5)_3\text{GeCN}^h$	B1	18°	213°	132
$(n\text{-C}_3\text{H}_7)_3\text{GeCN}^i$	A2	-13°	253°	132
$(\text{iso-C}_3\text{H}_7)_3\text{GeCN}$	A2	—	—	95
$(n\text{-C}_3\text{H}_9)_2\text{GeHCN}^j$	B5	—	$108^\circ\text{--}110^\circ/8$	133
$(\text{iso-C}_3\text{H}_7)_2\text{Ge}(\text{CN})_2$	A2	—	—	95
<i>Tin</i>				
$(\text{CH}_3)_3\text{SnCN}$	A2, B3	188°	—	30, 52, 111
$(\text{C}_2\text{H}_5)_3\text{SnCN}$	A2, B3	$163.5^\circ\text{--}164^\circ$	—	111, 134
$(n\text{-C}_3\text{H}_7)_3\text{SnCN}$	—	—	—	135
$(n\text{-C}_4\text{H}_9)_3\text{SnCN}$	A3, B3	$90^\circ\text{--}93^\circ$	—	111
$(\text{C}_6\text{H}_5)_3\text{SnCN}$	B1, B3	$255^\circ\text{--}256^\circ$	—	111, 136
$(\text{CH}_3)_2\text{Sn}(\text{CN})_2$	A3, B3	sol	—	11, 111
$(\text{C}_2\text{H}_5)_2\text{SnCN}$	—	—	—	135
$(\text{C}_2\text{H}_5)_2\text{Sn}(\text{CN})_2$	B3	—	—	111
$(n\text{-C}_3\text{H}_7)_2\text{Sn}(\text{CN})_2$	—	—	—	135
$(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{CN})_2$	B3	—	—	111
$(\text{C}_6\text{H}_5)_2\text{Sn}(\text{CN})_2$	B3	—	—	111
<i>Lead</i>				
$(\text{C}_2\text{H}_5)_3\text{PbCN}$	A2	189° dec	—	137
$(\text{iso-C}_3\text{H}_7)_3\text{PbCN}$	A2	135° dec	—	137

TABLE X—*continued*

Compound	Synthetic method ^a	M.p. ^b (°C)	B.p. ^b (°C)/mm	References
<i>Lead</i> —(continued)				
(C ₆ H ₅) ₃ PbCN	A1	250° dec	—	138
(C ₆ H ₅) ₂ Pb(OH)CN	B3	—	—	137
(C ₆ H ₅) ₂ Pb(CN) ₂	A2	245°–255° dec	—	137
<i>Arsenic</i>				
(CH ₃) ₂ AsCN	B1, C1	33°	140°; 159°/730	2, 139, 140
(CF ₃) ₂ AsCN	A2	—	89.5°	141
(ClCH=CH) ₂ AsCN	A1	—	120°/12	142
(C ₂ H ₅) ₂ AsCN	—	–50°	74°/12	18
(2-C ₄ H ₉ S) ₂ AsCN	A1	51°–55°	—	143
(2-C ₄ H ₉ O) ₂ AsCN	A2	32°	166°–167°/20	144
(iso-C ₄ H ₉) ₂ AsCN	—	—	116°/16	18
(2-ClC ₆ H ₄) ₂ AsCN	A1	85°–87°	—	143
(4-ClC ₆ H ₄) ₂ AsCN	A1	58°–60°	198°–200°	143
(3-NO ₂ C ₆ H ₄) ₂ AsCN	A1	151°–152°	—	145
(C ₆ H ₅) ₂ AsCN	A2	32°	200°/13.5	146
(2-CH ₃ C ₆ H ₄) ₂ AsCN	A1	74°	—	143
(3-CH ₃ C ₆ H ₄) ₂ AsCN	A1	43°–47°	—	143
(4-CH ₃ C ₆ H ₄) ₂ AsCN	A1	62°	—	143
(1-C ₁₀ H ₇) ₂ AsCN	A1	191°	—	143
(2-C ₁₀ H ₇) ₂ AsCN	A1	89°–91°	—	143
CH ₃ (ClCH=CH)AsCN	A1	oil	—	147
C ₂ H ₅ (C ₃ H ₇)AsCN	A2	—	110°–113°/27	139
C ₂ H ₅ (C ₄ H ₉)AsCN	A2	—	112°–112.5°/65	139
CH ₃ (3-NO ₂ C ₆ H ₄)AsCN	A2	79.5°–80.5°	—	148

$\text{CH}_3(\text{C}_6\text{H}_5)\text{AsCN}$	A1, C1	—	147°–148°/20	18, 148
$\text{C}_6\text{H}_5(\text{CH}=\text{CHCl})\text{AsCN}$	A2	—	—	149
$\text{C}_6\text{H}_5(2\text{-C}_4\text{H}_3\text{S})\text{AsCN}$	A1	49°–51°	168°–174°/0.5	143
$\text{CH}_3(1\text{-C}_{10}\text{H}_7)\text{AsCN}$	B4	85°	190°–191°/8	150
$\text{C}_6\text{H}_5(4\text{-ClC}_6\text{H}_4)\text{AsCN}$	A1	102°	—	143
$\text{C}_6\text{H}_5(2\text{-ClC}_6\text{H}_4)\text{AsCN}$	A1	40°–42°	—	143
$\text{C}_6\text{H}_5(2\text{-NH}_2\text{C}_6\text{H}_4)\text{AsCN}$	A1	53°	—	143
$\text{C}_6\text{H}_5(3\text{-NH}_2\text{H}_4)\text{AsCN}$	A1	114°	—	143
$(2\text{-ClC}_6\text{H}_4)(2\text{-CH}_3\text{C}_6\text{H}_4)\text{AsCN}$	A1	69°	—	143
$(3\text{-ClC}_6\text{H}_4)(2\text{-CH}_3\text{C}_6\text{H}_4)\text{AsCN}$	A1	64°	—	143
$(4\text{-ClC}_6\text{H}_4)(2\text{-CH}_3\text{C}_6\text{H}_4)\text{AsCN}$	A1	64°	—	143
$(2\text{-ClC}_6\text{H}_4)(4\text{-CH}_3\text{C}_6\text{H}_4)\text{AsCN}$	A1	oil	—	143
$(3\text{-ClC}_6\text{H}_4)(4\text{-CH}_3\text{C}_6\text{H}_4)\text{AsCN}$	A1	oil	—	143
$(4\text{-ClC}_6\text{H}_4)(4\text{-CH}_3\text{C}_6\text{H}_4)\text{AsCN}$	A1	oil	—	143
$(2\text{-NO}_2\text{C}_6\text{H}_4)(2\text{-CH}_3\text{C}_6\text{H}_4)\text{AsCN}$	A1	105°–107°	—	143
$(3\text{-NO}_2\text{C}_6\text{H}_4)(2\text{-CH}_3\text{C}_6\text{H}_4)\text{AsCN}$	A1	99°–101°	—	143
$(4\text{-NO}_2\text{C}_6\text{H}_4)(2\text{-CH}_3\text{C}_6\text{H}_4)\text{AsCN}$	A1	103°–105°	—	143
$(4\text{-NO}_2\text{C}_6\text{H}_4)(4\text{-CH}_3\text{C}_6\text{H}_4)\text{AsCN}$	A1	88°–90°	—	143
$\text{C}_6\text{H}_5(2\text{-CH}_3\text{C}_6\text{H}_4)\text{AsCN}$	A1	oil	—	143
$\text{C}_6\text{H}_5(3\text{-CH}_3\text{C}_6\text{H}_4)\text{AsCN}$	A1	oil	—	143
$\text{C}_6\text{H}_5(4\text{-CH}_3\text{C}_6\text{H}_4)\text{AsCN}$	A1	oil	—	143
$\text{C}_6\text{H}_5(3\text{-CH}_3\text{OC}_6\text{H}_4)\text{AsCN}$	A1	oil	—	143
$\text{C}_6\text{H}_5[3\text{-CH}_3\text{C}(\text{:O})\text{OC}_6\text{H}_4]\text{AsCN}$	A1	57°–59°	—	143
$\text{C}_6\text{H}_5[3\text{-CH}_3\text{OC}(\text{:O})\text{C}_6\text{H}_4]\text{AsCN}$	A1	oil	—	143
$\text{C}_6\text{H}_5[4\text{-CH}_3\text{OC}(\text{:O})\text{C}_6\text{H}_4]\text{AsCN}$	A1	oil	—	143
$(2\text{-CH}_3\text{C}_6\text{H}_4)(3\text{-CH}_3\text{C}_6\text{H}_4)\text{AsCN}$	A1	oil	—	143
$(2\text{-CH}_3\text{C}_6\text{H}_4)(4\text{-CH}_3\text{C}_6\text{H}_4)\text{AsCN}$	A1	oil	—	143
$(3\text{-CH}_3\text{C}_6\text{H}_4)(4\text{-CH}_3\text{C}_6\text{H}_4)\text{AsCN}$	A1	oil	—	143
$\text{C}_6\text{H}_5[2,4\text{-(CH}_3)_2\text{C}_6\text{H}_3]\text{AsCN}$	A1	oil	—	143
$(2\text{-CH}_3\text{C}_6\text{H}_4)[2,4\text{-(CH}_3)_2\text{C}_6\text{H}_3]\text{AsCN}$	A1	oil	—	143
$(4\text{-CH}_3\text{C}_6\text{H}_4)[2,4\text{-(CH}_3)_2\text{C}_6\text{H}_3]\text{AsCN}$	A1	oil	—	143

TABLE X—*continued*

Compound	Synthetic method ^a	M.p. ^b (°C)	B.p. ^b (°C)/mm	References
<i>Arsenic—(continued)</i>				
C ₆ H ₅ (1-C ₁₀ H ₇)AsCN	A1	98°–99°	—	143
C ₆ H ₅ (2-C ₁₀ H ₇)AsCN	A1	59°–61°	—	143
(4-CH ₃ C ₆ H ₄)(1-C ₁₀ H ₇)AsCN	A1	83°–84°	—	143
(4-CH ₃ C ₆ H ₄)(2-C ₁₀ H ₇)AsCN	A1	99°	—	143
(CH ₃) ₂ As(C ₆ H ₅)BrCN	B4	94°–96°	—	18
C ₆ H ₅ (CH ₃) ₂ AsICN	B4	93°	—	18
(C ₆ H ₅) ₃ AsBrCN	B4	130°–140°	—	151
(C ₆ H ₅) ₂ As(C ₂ H ₅)BrCN	B4	75°	—	151
(C ₆ H ₅) ₂ As(CH ₃)BrCN	B4	61°–62°	—	151
(C ₆ H ₅) ₂ AsCl ₂ CN	B4	130°–133°	—	152
(iso-C ₄ H ₉) ₂ As(C ₂ H ₅)BrCN	B4	69°	—	18
(C ₃ H ₇) ₂ As(C ₂ H ₅)BrCN	B4	—	—	18
(C ₂ H ₅) ₃ AsBrCN	B4	67°	—	18
CH ₃ As(CN) ₂	B1	116.5°	—	2, 140
<i>n</i> -C ₃ H ₇ As(CN) ₂	A2	82°–86°	—	139
<i>n</i> -C ₄ H ₉ As(CN) ₂	A2	61°–63°	—	139
<i>n</i> -C ₆ H ₁₁ As(CN) ₂	A2	69°–69.5°	—	139
<i>n</i> -C ₆ H ₁₃ As(CN) ₂	A2	67.8°–69.8°	—	139
2-C ₄ H ₉ OAs(CN) ₂	A2	105°	—	144
<i>Antimony</i>				
(CH ₃) ₂ SbCN	A1	113°–114°	—	153
C ₆ H ₅ (CH ₃)SbCN	C1	—	115°–120° high vac	25
(CH ₃) ₃ SbBrCN	B4	—	—	153
(CH ₃) ₃ SnICN	B4	174°	—	154
(CH ₃) ₂ Sb(C ₆ H ₅)BrCN	B4	135°	dec 150°	25

Bismuth

(C ₆ H ₅) ₂ BiCN	C1	210°	—	155, 156
(C ₆ H ₅) ₃ Bi(OH)CN	C2	135°	—	157
(C ₆ H ₅) ₃ Bi(CN) ₂	A1	—	—	158

Gold/Platinum

(CH ₃) ₃ PtCN	A3	sol	—	112
(C ₂ H ₅) ₂ AuCN	A2	103°–105°	—	100
(<i>n</i> -C ₃ H ₇) ₂ AuCN	A2	94°–95°	—	100
(<i>iso</i> -C ₃ H ₇) ₂ AuCN	—	88°–90°	—	159
(<i>iso</i> -C ₄ H ₉) ₂ AuCN	—	112°–113°	—	159
(<i>iso</i> -C ₅ H ₁₁) ₂ AuCN	—	70°	—	159
(cyclo-C ₆ H ₁₁) ₂ AuCN	—	152° dec	—	159

^a These numbers refer to the synthetic methods described in Section II. For example, B3 indicates Section II, B, 3.

^b sol, solid at room temperature; dec T°, decomposes at T° without melting; T° dec, melts at T° with decomposition; l., liquid at room temperature.

^c n^{20} 1.3883 (26°), d^{20} 0.7834 (93).

^d n^{20} 1.4270 (26°) (29, 93).

^e For supercooled liquid, n^{20} 1.4998, d^{20} 0.957 (128).

^f n^{20} 1.4349, d^{20} 0.830 (10).

^g n^{20} 1.4373 (30°) (27).

^h n^{20} 1.4509, d^{20} 1.111 (132).

ⁱ n^{20} 1.4544, d^{20} 1.041 (132).

^j n^{20} 1.4527, d^{20} 1.050 (133).

TABLE XI
ORGANOMETALLIC (Iso)CYANATES

Compound	Synthetic method ^a	M.p. ^b (°C)	B.p. (°C)/mm	n_D^{20}	d_4^{20}	References
<i>Mercury</i>						
C ₆ H ₅ HgNCO	B5	124°–125°	—	—	—	160
1-C ₄ H ₃ OHgNCO	B5	122°–123°	—	—	—	160
1-C ₄ H ₃ SHgNCO	B5	104°–105°	—	—	—	160
1,5-C ₄ H ₂ O(HgNCO) ₂	B5	sol	—	—	—	160
1,5-C ₄ H ₂ S(HgNCO) ₂	B5	sol	—	—	—	160
1,5-C ₄ H ₃ N(HgNCO) ₂	B5	sol	—	—	—	160
2-CH ₃ -1-C ₄ H ₂ OHgNCO	B5	114°–115°	—	—	—	160
2-CH ₃ -1-C ₄ H ₂ SHgNCO	B5	146°–146.5°	—	—	—	160
<i>Boron</i>						
(CH ₃) ₂ BNCO	A2	–118°	41° (extrap)	—	1.146 (–78°)	38
(C ₆ H ₅) ₂ BNCO	A1, A2	—	89°/0.01	1.6092	1.105	39, 161
C ₆ H ₅ B(NCO) ₂	A1, A2	—	60°/0.2	1.5527	1.187	39, 161
C ₆ H ₅ B[N(CH ₃) ₂]NCO	—	—	—	—	—	4
<i>Thallium</i>						
(CH ₃) ₂ TlNCO	A3	sol	—	—	—	46
(C ₆ H ₅) ₂ TlNCO	A1, C1	sol	—	—	—	46
<i>Silicon</i>						
(CH ₃) ₃ SiNCO	A1, A2, B5	–49°	91°	1.3960	0.867	162
(C ₂ H ₅) ₃ SiNCO	A2	—	165.1°	1.4295	0.889	163–165
(C ₆ H ₅) ₃ SiNCO	A2, B2	100°–102°	372°	—	—	15, 29, 166
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{COCH}_2\text{Si}(\text{CH}_3)_2\text{NCO} \end{array}$	A2	—	51°/12	1.4272	—	167

$(\text{CH}_3)_3\text{SiSi}(\text{CH}_3)_2\text{NCO}$	A2	—	160°	—	—	168
$\text{C}_6\text{H}_{11}\text{SiH}_2\text{NCO}$	A2	—	163.7°	1.4668	0.990	9
$(\text{CH}_3)_2\text{Si}(\text{NCO})_2$	A1	—31°	139°	1.4221	1.076	162
$(\text{C}_2\text{H}_5)_2\text{Si}(\text{NCO})_2$	A2	—	176.7°	1.4348	1.022	163–165
$(n\text{-C}_4\text{H}_9)_2\text{Si}(\text{NCO})_2$	B3	—	96°/3	1.4228 (26.5°)	—	169
$(\text{C}_6\text{H}_5)_2\text{Si}(\text{NCO})_2$	A2	23°	320°	1.5675	1.188	166
$\text{CH}_3\text{Si}(\text{NCO})_3$	A1	2.7°	170.8°/179	1.4430	1.267	162
$\text{C}_2\text{H}_5\text{Si}(\text{NCO})_3$	A2	—	183.5°	1.4468	1.219	163–165
$n\text{-C}_3\text{H}_7\text{Si}(\text{NCO})_3$	A2	—	192.2°	1.4462	1.173	165
$\text{iso-C}_3\text{H}_7\text{Si}(\text{NCO})_3$	A2	—	192°	1.4444	1.163	165
$n\text{-C}_4\text{H}_9\text{Si}(\text{NCO})_3$	A2	—37°	215.5°	1.4479	1.141	162
$\text{C}_6\text{H}_{11}\text{Si}(\text{NCO})_3$	A2	—	253°	1.4787	1.208	9
$\text{C}_7\text{H}_{15}\text{Si}(\text{NCO})_3$	A2	—	258°	1.4516	1.077	10
<i>Germanium</i>						
$(\text{CH}_3)_3\text{GeNCO}$	A1, A2	—	122°	—	—	37
$(\text{C}_2\text{H}_5)_3\text{GeNCO}$	A2	—26.4°	200°	1.454	—	170
$(n\text{-C}_3\text{H}_7)_3\text{GeNCO}$	A2	—19°	247°	1.4575	1.055	132
$(\text{iso-C}_3\text{H}_7)_3\text{GeNCO}$	A2	—	238°	1.4602	1.097	171
$(n\text{-C}_4\text{H}_9)_3\text{GeNCO}$	A2	—47°	283°	1.4595	1.044	172
$(\text{C}_2\text{H}_5)_2\text{Ge}(\text{NCO})_2$	A2	—32°	226°	—	—	173
$(\text{iso-C}_3\text{H}_7)_2\text{Ge}(\text{NCO})_2$	A2	—	239°	1.464	1.225	95
$(n\text{-C}_4\text{H}_9)_2\text{Ge}(\text{NCO})_2$	A2	—	273°	1.4634	1.179	133
$\text{C}_2\text{H}_5\text{Ge}(\text{NCO})_3$	A2	—31°	225°	—	—	173
<i>Tin</i>						
$(\text{CH}_3)_3\text{SnNCO}$	A2	105°–107°	—	—	—	37
$(\text{C}_2\text{H}_5)_3\text{SnNCO}$	A2, B1	48°; 51°–53°	239°	—	—	14, 135
$(n\text{-C}_4\text{H}_9)_3\text{SnNCO}$	A2, B2, B3	—	112°–115°/0.5 144°–147°/1.3	1.4885; 1.490 (22°)	—	14, 28
$(\text{iso-C}_4\text{H}_9)_3\text{SnNCO}$	B1, B2	—	103°/0.3	1.489 (21°)	—	14
$(\text{C}_6\text{H}_5)_3\text{SnNCO}$	A2, B2	100°	—	—	—	28, 174

TABLE XI—*continued*

Compound	Synthetic method ^a	M.p. ^b (°C)	B.p. (°C)/mm	n_D^{20}	d_4^{20}	References
<i>Tin</i> —(continued)						
(CH ₃) ₂ Sn(NCO) ₂	A3	sol	—	—	—	11
(<i>n</i> -C ₄ H ₉) ₂ Sn(NCO) ₂	A2	48°–51°	—	—	—	28
[(<i>n</i> -C ₄ H ₉) ₂ SnNCO] ₂ O	B2	195°–215°	—	—	—	14
[(C ₆ H ₅) ₂ SnNCO] ₂ O	C2	158°–162°	—	—	—	28
(C ₆ H ₅) ₂ Sn[OSn(OH)(C ₆ H ₅) ₂]NCO	C2	300°–301°	—	—	—	28
<i>Lead</i>						
(CH ₃) ₃ PbNCO	A2	dec 220°	—	—	—	37
(C ₂ H ₅) ₃ PbNCO	B1	—	—	—	—	137
<i>Arsenic</i>						
(C ₆ H ₅) ₂ As(NCO) ₂	B2	40°	—	—	—	14
<i>Antimony</i>						
(<i>n</i> -C ₄ H ₉) ₃ Sb(NCO) ₂	B1, B2	dec 190°	—	—	—	14
(<i>iso</i> -C ₄ H ₉) ₃ Sb(NCO) ₂	A1	—	122°–124°/0.15	1.5128	—	14
(C ₆ H ₅) ₃ Sb(NCO) ₂	A2	111°–112°	—	—	—	175
<i>Bismuth</i>						
(C ₆ H ₅) ₃ Bi(NCO) ₂	A1	129°	—	—	—	158

^a See footnote *a*, Table X.^b sol, solid at room temperature; dec T°, decomposes at T° without melting; extrap, extrapolated.

TABLE XII
ORGANOMETALLIC (ISO)THIOCYANATES

Compound	Synthetic method ^a	M.p. ^b (°C)	B.p. (°C)/mm	n_D^{20}	d_4^{20}	References
<i>Mercury</i>						
CH ₃ HgNCS	B1	—	—	—	—	176
C ₂ H ₅ HgNCS	A3	—	—	—	—	177
C ₆ H ₅ HgNCS	A3, B4, B5	231°–232.5°	—	—	—	124
<i>p</i> -CH ₃ OC ₆ H ₄ HgNCS	B5	208°	—	—	—	125
1-C ₁₀ H ₇ HgNCS	B5	—	—	—	—	127
<i>Boron</i>						
C ₆ H ₅ B(OC ₄ H ₉ - <i>n</i>)NCS	A1	—	94°–100°/0.6	—	—	178
(C ₆ H ₅) ₂ BNCS	A2	—	114°–116°/0.2	1.6714	1.119	39
C ₆ H ₅ B[N(CH ₃) ₂]NCS	A2	—	—	—	—	4
<i>Thallium</i>						
(CH ₃) ₂ TlNCS	A1, B1	sol	—	—	—	126a, 179
(C ₂ H ₅) ₂ TlNCS	A2	—	—	—	—	126
C ₆ H ₅ Tl(NCS) ₂	A2	—	—	—	—	24
<i>Silicon</i>						
(CH ₃) ₃ SiNCS	1A, 1B	–32.8°	143.1°	1.4820	0.9257	74
(C ₂ H ₅) ₃ SiNCS	1B	—	210.5°	1.4948	0.9385	180
(C ₆ H ₅) ₃ SiNCS	A2, B2	99°–100°	396°	—	—	15, 181
(CH ₃) ₂ C ₆ H ₅ SiNCS	A2, C3	—	252°–254°	1.5556(30°)	1.0384(30°)	128
(CH ₃) ₂ SiHNCS	A2	—	0°/8 dec	—	—	130
CH ₃ SiH ₂ NCS	A2	—	—	—	—	129

TABLE XII—continued

Compound	Synthetic method ^a	M.p. ^b (°C)	B.p. (°C)/mm	n_D^{20}	d_4^{20}	References
<i>Silicon</i> —(continued)						
C ₆ H ₁₁ SiH ₂ NCS	A2	—	348°	1.6179	1.231	9
C ₇ H ₁₅ SiH ₂ NCS	A2	—	231°	1.5336	1.081	10
(CH ₃) ₂ Si(NCS) ₂	A1	18°	216°	1.5661	1.1416	42, 165
(C ₂ H ₅) ₂ Si(NCS) ₂	A2	—	245.5°	1.5446	1.0937	180
(C ₆ H ₅) ₂ Si(NCS) ₂	A2	46°	376°	—	—	181
CH ₃ Si(NCS) ₃	A1	73°	267.5°	—	1.340	42, 74
C ₂ H ₅ Si(NCS) ₃	A2	—	276°	1.6195	1.264	163
<i>n</i> -C ₃ H ₇ Si(NCS) ₃	A2	—	289.5°	1.6104	1.2248	85, 165
CH ₂ =CHSi(NCS) ₃	A1	—	134°–138°/3	1.6350(26°)	—	182
CH ₂ =CHCH ₂ Si(NCS) ₃	A1	—	126°–128°/2.5	1.6140(26°)	—	182
<i>n</i> -C ₄ H ₉ Si(NCS) ₃	A2	–0.5°	300.6°	1.5928	1.189	164
C ₆ H ₁₁ Si(NCS) ₃	A2	—	348°	1.6179	1.231	9
C ₆ H ₅ Si(NCS) ₃	A2	52°	339.6°	—	1.30	181
C ₆ H ₅ CH ₂ Si(NCS) ₃	A2	36°	348.9°	—	1.28	164, 180
<i>p</i> -CH ₃ C ₆ H ₅ Si(NCS) ₃	A1	—	182°–185°/3.5	1.6490(26°)	1.6490(26°)	182
<i>n</i> -C ₇ H ₁₅ Si(NCS) ₃	A2	—	347°	1.5739	1.129	10
<i>Germanium</i>						
(CH ₃) ₃ GeNCS	B1, D3	38°–38.5°	191.5°–193°	1.4960	—	30
(C ₂ H ₅) ₃ GeNCS	A2	–46°	252°	1.517	1.184	132
(<i>n</i> -C ₃ H ₇) ₃ GeNCS	A2	–56°	287°	1.5063	1.105	132
(<i>iso</i> -C ₃ H ₇) ₃ GeNCS	A2	18°	277°	1.512	1.112	183
(<i>n</i> -C ₄ H ₉) ₃ GeNCS	A2	—	319°	1.5039	1.071	132
(CH ₃) ₂ Ge(NCS) ₂	A1	45.5°–47°	266°–268°	—	—	184
(C ₂ H ₅) ₂ Ge(NCS) ₂	A2	16°	298°	—	1.356	132

(iso-C ₃ H ₇) ₂ Ge(NCS) ₂	A2	—	296°	1.558	1.234	95
(n-C ₄ H ₉) ₂ Ge(NCS) ₂	A2	—	337°	1.5501	1.201	133
C ₂ H ₅ Ge(NCS) ₃	B1	—	308°	—	—	132
(n-C ₄ H ₉) ₂ GeHNCS	D1	—	96°–98°/1	1.5097	1.123	133
<i>Tin</i>						
(CH ₃) ₃ SnNCS	A1	107°–110°	—	—	—	30, 37
(C ₂ H ₅) ₃ SnNCS	—	33°	282° dec	—	—	135
(n-C ₄ H ₉) ₃ SnNCS	A2, A3	—	160°–162°/0.8	1.543	1.235	60
(C ₆ H ₅) ₃ SnNCS	A2	172°–173°	—	—	—	174
(CH ₃) ₂ Sn(NCS) ₂	A3	sol	—	—	—	11
(CH ₂ =CH) ₂ Sn(NCS) ₂	—	163.5°–165°	—	—	—	135
(C ₂ H ₅) ₂ Sn(NCS) ₂	—	—	—	—	—	135
(n-C ₃ H ₇) ₂ Sn(NCS) ₂	A3	135°–136°	—	—	—	80
(n-C ₄ H ₉) ₂ Sn(NCS) ₂	A1	145°	—	—	—	80
(C ₂ H ₅) ₂ Sn[OSn(OH)(C ₂ H ₅) ₂]NCS	A1	170°–176° dec	—	—	—	80
[(C ₂ H ₅) ₂ Sn(NCS)] ₂ O	B5	178°–179°	—	—	—	80
(CH ₃) ₂ Sn(OC ₉ H ₆ N)NCS	B5, C2	123°–124°	—	—	—	81
(n-C ₃ H ₇) ₂ Sn[OSn(OH)(n-C ₃ H ₇) ₂]NCS	A1	162°–167° dec	—	—	—	80
[(n-C ₃ H ₇) ₂ Sn(NCS)] ₂ O	B5	108°	—	—	—	80
(n-C ₃ H ₇) ₂ Sn(OC ₉ H ₆ N)NCS	B5, C2	144°	—	—	—	81
(n-C ₄ H ₉) ₂ Sn[OSn(OH)(n-C ₄ H ₉) ₂]NCS	A1	123°–139° dec	—	—	—	82
[(n-C ₄ H ₉) ₂ Sn(NCS)] ₂ O	B5	84°	—	—	—	82
<i>Lead</i>						
(CH ₃) ₃ PbNCS	A1	dec 145°	—	—	—	37
(C ₂ H ₅) ₃ PbNCS	B1	35°	—	—	—	137
(C ₆ H ₅) ₃ PbNCS	A1	dec 230°	—	—	—	138
(C ₆ H ₅) ₂ Pb(NCS) ₂	B1	—	—	—	—	137
<i>Arsenic</i>						
(CH ₃) ₂ AsNCS	A1	—	92°/17	—	—	184a
(CF ₃) ₂ AsNCS	B1	—	117°	1.445	—	141

TABLE XII—*continued*

Compound	Synthetic method ^a	M.p. ^b (°C)	B.p. (°C)/mm	n_D^{20}	d_4^{20}	References
<i>Arsenic—(continued)</i>						
$n\text{-C}_3\text{H}_7\text{As}(\text{C}_2\text{H}_5)\text{NCS}$	A1	—	102°–110°/0.65	—	—	139
$\text{C}_6\text{H}_5\text{As}(\text{CH}_3)\text{NCS}$	A1	—	176°–179°/18	—	—	148
$\text{CH}_3\text{As}(1\text{-C}_{50}\text{H}_7)\text{NCS}$	A1	50°–50.5°	211°–213°/8	—	—	150
$(3\text{-NO}_2\text{C}_6\text{H}_4)_2\text{AsNCS}$	A1	103°–105°	—	—	—	145
$(\text{C}_6\text{H}_5)_2\text{AsNCS}$	A1	—	230°–233°/22	—	—	185
<i>Antimony</i>						
$(\text{C}_6\text{H}_5)_3\text{Sb}(\text{OH})\text{NCS}$	C2	—	—	—	—	175
$(\text{CH}_3)_3\text{Sn}(\text{NCS})_2$	A1	—	—	—	—	154
$(\text{C}_6\text{H}_5)_3\text{Sb}(\text{NCS})_2$	A2	105°–106°	—	—	—	175
<i>Bismuth</i>						
$(\text{C}_6\text{H}_5)_2\text{BiNCS}$	B3	122°–125°	—	—	—	185
$\text{C}_6\text{H}_5\text{Bi}(\text{NCS})_2$	—	186°	—	—	—	157
$(\text{C}_6\text{H}_5)_3\text{Bi}(\text{NCS})_2$	A1	—	—	—	—	158
<i>Gold</i>						
$[(\text{C}_2\text{H}_5)_2\text{AuSCN}]_2$	A2	62°–64°	—	—	—	110

^a See footnote *a*, Table X.^b sol, solid at room temperature; dec T°, decomposes at T° C without melting; T° dec, melts at T° with decomposition.

TABLE XIII
ORGANOMETALLIC AZIDES

Compound	Synthetic method ^a	M.p. ^b (°C)	B.p. (°C)/mm	n_D^{20}	References
<i>Cadmium</i>					
CH ₃ CdN ₃	B4	sol	—	—	20a
<i>Mercury</i>					
CH ₃ HgN ₃	B1	130.5°	dec 200°	—	3, 176
C ₂ H ₅ HgN ₃	B1	151°–153°	—	—	3
C ₆ H ₅ HgN ₃	B1	154°–155°	—	—	3
C ₆ H ₅ CH ₂ HgN ₃	A1	120° dec	—	—	185a
<i>Boron</i>					
(C ₂ H ₅) ₂ BN ₃	B5, C3	—	—	—	3, 23
(C ₆ H ₅) ₂ BN ₃	A1	—	109°–111°/high vac	—	3, 186
[2,4,6-(CH ₃) ₃ C ₆ H ₂] ₂ BN ₃	A1	liq	—	—	3, 5
C ₂ H ₅ B(N ₃) ₂	B5	—	—	—	3, 23
<i>Aluminum</i>					
(C ₂ H ₅) ₂ AlN ₃	A1	liq	—	—	3, 107
CH ₃ Al(N ₃) ₂	B3	sol	—	—	3, 17
<i>Thallium</i>					
(CH ₃) ₂ TlN ₃	A3	sol	—	—	3, 12
(C ₆ H ₅) ₂ TlN ₃	A3	dec 321°	—	—	185a
C ₆ H ₅ Tl(N ₃) ₂	B1	dec 200°	—	—	3, 24

TABLE XIII—*continued*

Compound	Synthetic method ^a	M.p. ^b (°C)	B.p. (°C)/mm	n_D^{20}	References
<i>Silicon</i>					
(CH ₃) ₃ SiN ₃	A1, A2, B3, B5	−95°	94°	1.4161 (d_4^{20} 0.8763)	3, 6, 7, 13, 22, 26, 35, 117, 187, 188–190
(C ₂ H ₅) ₃ SiN ₃	A1	—	39°/5; 100°–104°/95	—	3, 44, 190
(<i>n</i> -C ₄ H ₉) ₃ SiN ₃	A1	—	88°/0.001	—	3, 190
(C ₆ H ₅) ₃ SiN ₃	A1	81°	—	—	3, 7, 8, 35, 189, 191, 192
(CH ₃) ₅ Si ₂ N ₃	A1	—	158°–160°	—	3, 44
(CH ₃) ₂ Si(C ₆ H ₅)N ₃	A1, B3	—	89°/11	1.5189	3, 44, 187
[2,4,6-(CH ₃) ₃ C ₆ H ₂]Si(CH ₃) ₂ N ₃	A1	65°–68°	—	—	3, 190
(C ₆ H ₅) ₂ Si(CH ₃)N ₃	A1, B5	—	196°–198°/47 112°/0.4	1.5779	3, 44, 187
1-C ₆ H ₅ C ₆ H ₄ Si(CH ₃) ₂ N ₃	A1	—	152°/6.5	1.5745	3, 34
CH ₃ SiCl ₂ N ₃	B5	—	100.5°	—	3, 22
(CH ₃) ₂ SiClN ₃	B5	—	120°	—	3, 22
(CH ₃) ₂ Si(NHC ₄ H ₉ - <i>n</i>)N ₃	B3, B5	—	75°/20	1.4409	3, 187
(CH ₃) ₂ Si(N ₃) ₂	A1, B5	—	144.3°	1.4579 (d_4^{20} 1.0845)	3, 8, 22, 187
(C ₆ H ₅) ₂ Si(N ₃) ₂	A1, B5	—	85°–90°/0.001	1.5887	3, 8, 22, 192
CH ₃ SiCl(N ₃) ₂	B5	—	47°/20	—	3, 22
CH ₃ Si(N ₃) ₃	B5	—	70°–73°/20	—	3, 22
C ₆ H ₅ Si(N ₃) ₃	B5	—	63°/0.001	—	3, 22
1,4-(N ₃) ₃ SiC ₆ H ₄ Si(N ₃) ₃	A1	—	—	—	192a
<i>Germanium</i>					
(CH ₃) ₃ GeN ₃	A1, B1	−65°	136°	—	3, 13, 37, 193
(C ₆ H ₅) ₃ GeN ₃	A1, B1	102°–103°	—	—	3, 44, 187

$(\text{CH}_3)_2\text{Ge}(\text{N}_3)_2$	A1	-14°	$43.5^\circ/2$	—	3, 193
$\text{C}_6\text{H}_5\text{Ge}(\text{N}_3)_3$	A1	—	—	—	192a
<i>Tin</i>					
$(\text{CH}_3)_3\text{SnN}_3$	B1	$120^\circ-121^\circ$	—	—	3, 13, 37, 113, 119
$(n\text{-C}_4\text{H}_9)_3\text{SnN}_3$	B1	—	$118^\circ-120^\circ/0.18$	1.5097	3, 113, 119
$(\text{C}_6\text{H}_5)_3\text{SnN}_3$	B1	$112^\circ; 115^\circ-116^\circ$	—	—	3, 8, 25, 44, 113, 119
$(o\text{-CH}_3\text{C}_6\text{H}_4)_3\text{SnN}_3$	B1	81°	—	—	193a
$(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{SnN}_3$	B1	115°	—	—	193a
$(\text{C}_6\text{H}_5\text{CH}_2)_3\text{SnN}_3$	B1	119°	—	—	193a
$[\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{CH}_2]_3\text{SnN}_3$	B1	$96^\circ-96.5^\circ$	—	—	3, 194
$(\text{CH}_3)_2\text{Sn}(\text{N}_3)_2$	A3	sol	—	—	3, 11, 44
<i>Lead</i>					
$(\text{CH}_3)_3\text{PbN}_3$	B1	dec 165°	—	—	3, 13, 37
$(\text{C}_6\text{H}_5)_3\text{PbN}_3$	B1	dec 185°	—	—	3, 8, 35, 195, 196
$(\text{C}_6\text{H}_5)_2\text{Pb}(\text{N}_3)_2$	B1	dec 145°	—	—	3, 196
<i>Arsenic</i>					
$(\text{C}_6\text{H}_5)_2\text{AsN}_3$	A1	sol	—	—	3, 33
<i>Antimony</i>					
$(\text{C}_6\text{H}_5)_2\text{SbN}_3$	—	dec 200°	—	—	3, 197
$(\text{C}_6\text{H}_5)_3\text{Sb}(\text{N}_3)_2$	B1	138°	—	—	3, 44
<i>Bismuth</i>					
$(\text{C}_6\text{H}_5)_2\text{BiN}_3$	C1	168°	—	—	3, 24
$(\text{C}_6\text{H}_5)_3\text{Bi}(\text{OH})\text{N}_3$	B1	—	—	—	3, 24
$(\text{C}_6\text{H}_5)_3\text{Bi}(\text{N}_3)_2$	A1	95°	dec 100°	—	3, 24

^a See footnote *a*, Table X.

^b sol, solid at room temperature; liq, liquid at room temperature; dec T° , decomposes at T° without melting.

TABLE XIV
 ORGANOMETALLIC FULMINATES

Compound	Synthetic method ^a	M.p. ^b (°C)	References
<i>Mercury</i>			
C ₆ H ₅ HgCNO	B5	178° dec	46
<i>o</i> -CH ₃ C ₆ H ₄ HgCNO	B5	155° dec	46
C ₆ H ₅ CH ₂ HgCNO	A1	103°–106° dec	46
1-C ₁₀ H ₇ HgCNO	B5	156°–157° dec	46
<i>Thallium</i>			
(CH ₃) ₂ TlCNO	A3	Explodes	46
(C ₆ H ₅) ₂ TlCNO	A3	290°–305° dec	44
<i>Silicon</i>			
(CH ₃) ₃ SiCNO	A2	Polymerizes	36
(C ₆ H ₅) ₃ SiCNO	A2	105° dec	36
<i>Germanium</i>			
(C ₆ H ₅) ₃ GeCNO	A2	122°–124° dec	36
<i>Tin</i>			
(C ₆ H ₅) ₃ SnCNO	A1	146°–148° dec	36
<i>Lead</i>			
(<i>n</i> -C ₃ H ₇) ₃ PbCNO	B1	sol	36
(C ₆ H ₅) ₃ PbCNO	B1	174°–175° dec	36

^a See footnote *a*, Table X.^b sol, solid at room temperature; T° dec, melts at T° with decomposition.
 TABLE XV
 ORGANOMETALLIC (ISO)SELENOCYANATES

Compound	Synthetic method ^a	M.p. ^b (°C)	B.p. (°C)/mm	References
<i>Mercury</i>				
CH ₃ HgSeCN	B4, B5	dec 60°	—	43
C ₆ H ₅ HgSeCN	B4, B5	dec 100°	—	43
<i>Silicon</i>				
(CH ₃) ₃ SiNCSe	A1	—	175°–177°	44

TABLE¹ XV—continued

Compound	Synthetic method ^a	M.p. ^b (°C)	B.p. (°C)/mm	References
<i>Tin</i>				
(CH ₃) ₃ SnNCSe	A1	sol	—	44
(C ₆ H ₅) ₃ SnNCSe	—	sol	—	45
<i>Lead</i>				
(CH ₃) ₃ PbSeCN	B4	sol	—	44
(C ₂ H ₅) ₃ PbSeCN	A1, A2	33–34°	—	137, 18
(C ₆ H ₅) ₃ PbSeCN	A1, B4	sol	—	45
(C ₆ H ₅) ₃ Pb(SeCN) ₂	B4	sol	—	45
<i>Bismuth</i>				
(C ₆ H ₅) ₂ BiSeCN	B4	dec 25°	—	19
(<i>p</i> -CH ₃ C ₆ H ₄) ₂ BiSeCN	B4	dec 25°	—	19

^a See footnote a, Table X.^b sol, solid at room temperature; dec T°, decomposes at T° without melting.

ACKNOWLEDGMENTS

For generously supplying information in advance of publication, the authors are grateful to Drs. Doyle Britton, Velmer Fassel, N. S. Greenwood, Michael Lappert, Walter Reichle, and Dietmar Seyferth. We also acknowledge helpful conversations with Drs. Evelyn Ebsworth and Richard F. Fenske.

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Insertion Reactions of Compounds of Metals and Metalloids Involving Unsaturated Substrates

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I. Introduction	225
II. Classification of Insertion Reactions and General Considerations	226
III. 1,2-Addition of Metal Complexes to Unsaturated Substrates	237
A. Insertion Reactions of Alkenes and Alkynes (also 1,4-Addition)	237
B. Insertion Reactions of Isocyanates, Isothiocyanates, Carbodiimides, Ketene, and Diketene	243
C. Insertion Reactions of Carbon Dioxide, Carbonyl Sulfide, Carbon Disulfide, and <i>N</i> -Thionylamides	247
D. Insertion Reactions of Sulfur Trioxide, Selenium Trioxide, and Sulfur Dioxide	248
E. Insertion Reactions of Aldehydes and Ketones	249
F. Insertion Reactions of Nitric Oxide, Dinitrogen Tetroxide, Nitrosobenzene, and Nitromethane	251
G. Insertion Reactions of Nitriles	252
IV. 1,1-Addition of Metal Complexes to Unsaturated Substrates	253
A. Insertion Reactions of Isonitriles	253
B. Insertion Reactions of Carbon Monoxide	254
V. Tabular Survey	257
References	310

I

INTRODUCTION

Very many reactions, especially significant in organometallic chemistry, are now known which may broadly be described as insertions. Historically, they stem from the experiments of Berthelot and Jungfleisch in 1869 (14-16), on the reactions between acetylene and antimony(V) chloride to afford 2-chlorovinylantimony chlorides $(\text{ClCH}=\text{CH})_2\text{SbCl}_3$ and $(\text{ClCH}=\text{CH})_3\text{SbCl}_2$.

This review has a twofold aim. On the one hand, we wish to draw together a vast amount of apparently unrelated observations, then to lend some system to the field by indicating the limited number of basic patterns which have emerged (see Section II), and finally more closely to examine individual classes of reactions; it will be made apparent that main group element complexes do not behave significantly differently, except in detail, from those of transition metals. Secondly, we have made an attempt (see Section V) comprehensively (within arbitrary limits defined in Section II) to tabulate data on individual insertion reactions, which clearly provide pointers to the enormous possibilities for further research.

Insertion reactions seem to be important for at least the following reasons:

(1) Their use provides elegant and facile syntheses for a wide variety of organometallic compounds, especially those having functional groups. These are either not accessible by alternative routes, or are less conveniently so obtained [e.g., for dithiocarbamates, Eq. (11)].

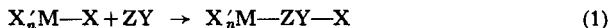
(2) In identifying their role, many important processes, particularly catalytic processes, are better understood.

II

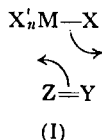
CLASSIFICATION OF INSERTION REACTIONS AND GENERAL CONSIDERATIONS

Insertion reactions of metal (M) complexes of type $X_n'M-X$ may be classified according to the nature of the inserting group. This may be one of the types (a)–(c) described below. The M–X bonds which have been shown to be susceptible to such cleavage are M–H, M–Hal, M–O, M–S, M–N, M–P, M–C, M–M, and M–M'. We shall refer to the group X as the migrating group, and X may be hydrogen, halogen, alkoxy, aryloxy, carboxylate, thioalkyl, thioaryl, dithiocarbamato, amino, hydrazino, carbamato, amidino, guanidino, ureido, phosphino, alkyl, alkenyl, alkynyl, aryl, organometallic groups such as $-SiMe_3$ and $-Mn(CO)_5$, and groups of the type $-MX_n'$ such as $-BCl_2$.

(a) *1,2-Addition to an unsaturated substrate ZY (doubly or triply bonded).* The general form of the reaction is then given by Eq. (1)



and is exemplified for each of the 23 such reagents (or classes of reagents, for organic compounds) which have been encountered so far by Eqs. (2)–(23). As a convenient formalism, we may picture these as involving a cyclic transition state (I).



This is undoubtedly a gross oversimplification, especially so since unsaturated hydrocarbons are for the most part susceptible only to electrophilic reagents, whereas the other substrates generally respond to attack by nucleophiles. The majority of the reactions may be regarded as 1,2-dipolar additions. It is to be anticipated that a further, but more restricted, class of reactions will be discovered which are *1,3-dipolar additions*, by utilizing substrates such as $\text{R}-\text{C}\equiv\text{N}^+-\text{O}^- \leftrightarrow \text{R}-\text{C}^+=\text{N}-\text{O}^-$ (144a). A few *1,4-addition reactions* are also known, whereby a metal complex adds to a conjugated polyunsaturated reagent [e.g., see Eq. (24)].

A process related to (1,2), (1,4), or (1,5) additions is *ring opening*. This has been most thoroughly explored for reactions of BCl_3 with cyclic ethers [Eq. (24a)] (82c). Similarly, $\text{Zr}(\text{NMe}_2)_4$ and an excess of ethylene oxide gave $(\text{Me}_2\text{N})_2\text{Zr}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_2$ (61a).

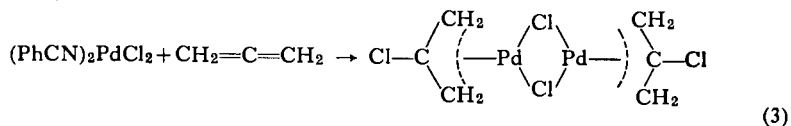
Alkenes:

(Table I)



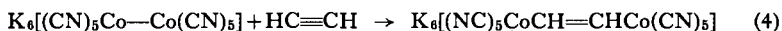
Allenes:

(Table I)



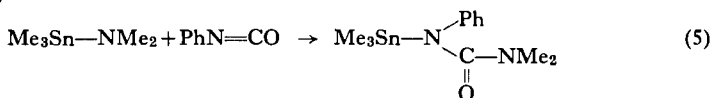
Alkynes:

(Table I)



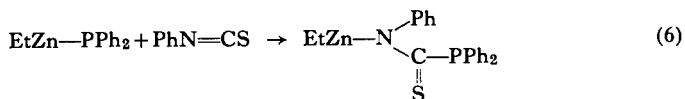
Isocyanates:

(Table II)

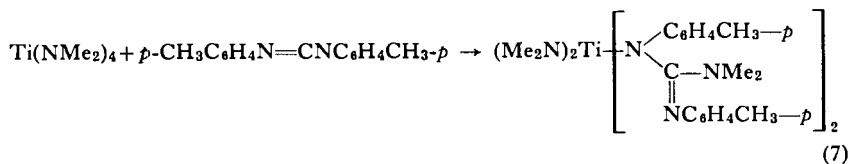


Isothiocyanates:

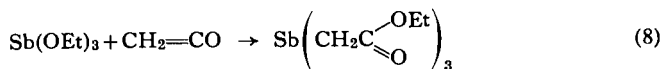
(Table II)

*Carbodiimides:*

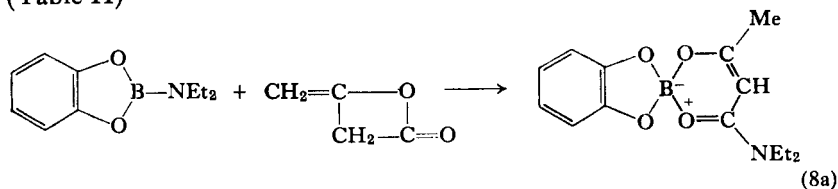
(Table II)

*Ketenes:*

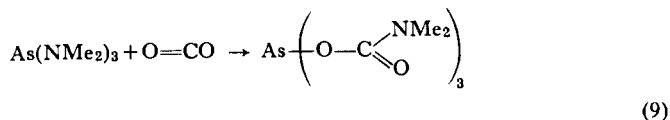
(Table II)

*Diketene:*

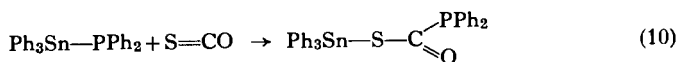
(Table II)

*Carbon dioxide:*

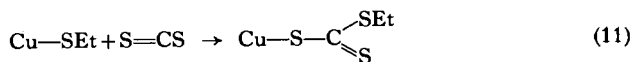
(Table III)

*Carbonyl sulfide:*

(Table III)

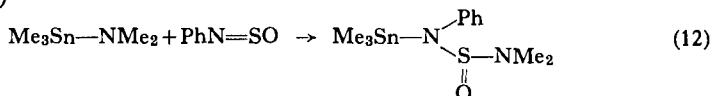
*Carbon disulfide:*

(Table III)

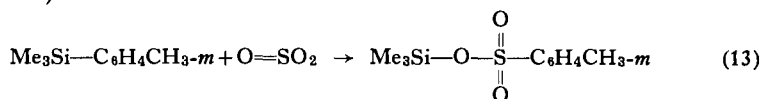


N-Thionylamides:

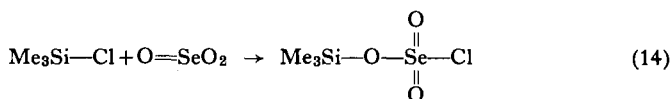
(Table III)

*Sulfur trioxide:*

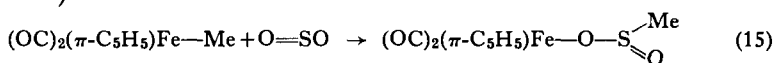
(Table IV)

*Selenium trioxide:*

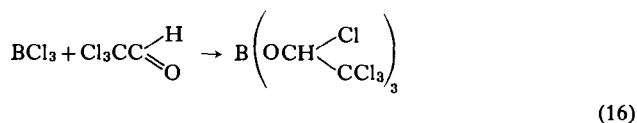
(Table IV)

*Sulfur dioxide:*

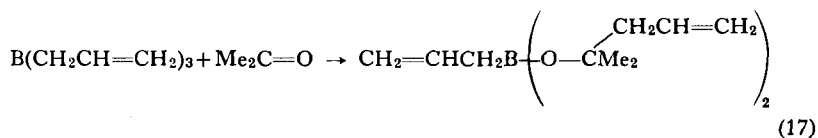
(Table IV)

*Aldehydes:*

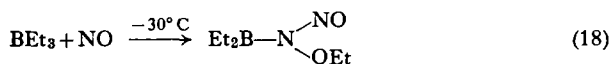
(Table V)

*Ketones:*

(Table V)

*Nitric oxide:*

(Table VI)

*Dinitrogen tetroxide:*

(Table VI)

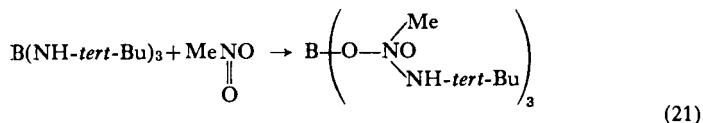


Nitroso compounds:

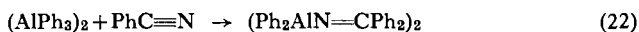
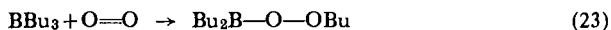
(Table VI)

*Nitro compounds:*

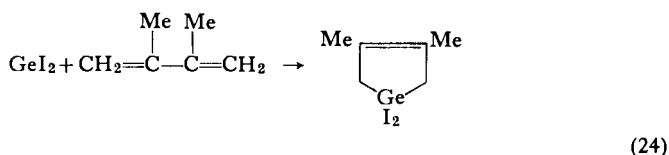
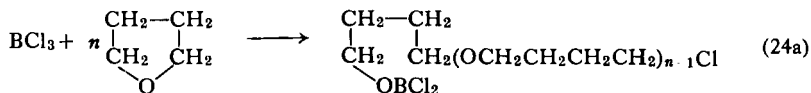
(Table VI)

*Nitriles:*

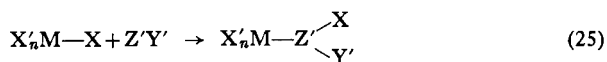
(Table VII)

*Oxygen:**1,4-Addition:*

(Table I)

*Ring opening:*

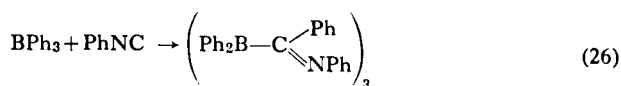
(b) *1,1-Addition to an unsaturated substrate Z'Y'*. The general form of the reaction is given by Eq. (25)



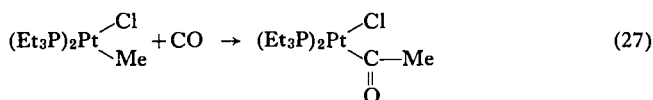
and is exemplified by Eqs. (26)–(28) for isonitrile and carbon monoxide insertion reactions. We divide carbonylations into two types. This may, however, be mechanistically unnecessary. In the first [e.g., Eq. (27)], an intramolecular rearrangement is indicated either from the stoichiometry or, in one case only, by a labeling experiment [Eq. (29)] (66). In the second [e.g., Eq. (28)], an M—CO compound is not isolated, but may nevertheless be a transient intermediate.

Isonitriles:

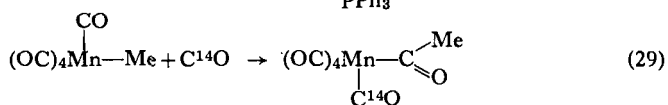
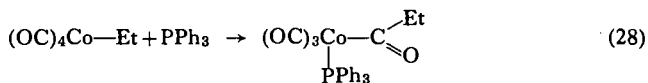
(Table VIII)

*Carbon monoxide:*

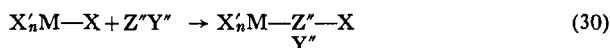
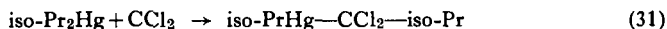
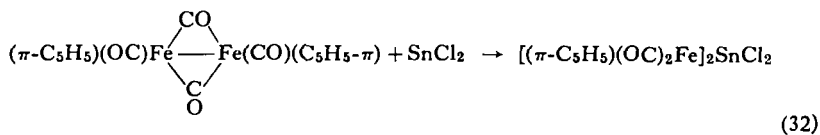
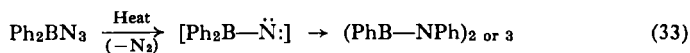
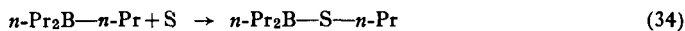
(Table IX)

*Carbon monoxide (intramolecular):*

(Table X)

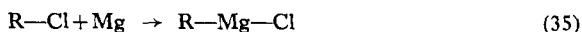


(c) *Oxidative 1,1-addition to low coordination number compounds, transient species, or atoms.* The general form of the reaction is given by Eq. (30), and is exemplified by Eqs. (31)–(36).

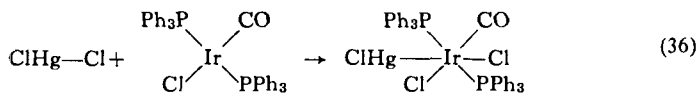
*Carbene:**M'X₂ (M' = Si, Ge, Sn, or Pb):**Nitrene:**Nonmetals (S, Se, P):*

Metals (Mg, Al, Si, Ge, Sn, Pb, etc.):

("Direct" synthesis of organometallics)



Square planar complexes:



In order to keep this review within manageable size, we propose to limit our further discussion by imposing the following restrictions:

(1) Insertion reactions into C—X, N—X, P—X, S—X, and halogen—X bonds are excluded. It can be argued that the products are, in any case, not organometallic.

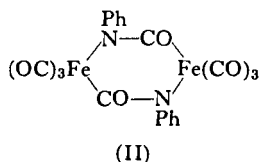
(2) Insertion reactions into M—X bonds where M is a Group II metal (Be, Mg, Zn, Cd, or Hg) are not discussed in detail. The best known of these are the Grignard (160a) and mercuration (61a, 179a) reactions, which are well-documented elsewhere. Likewise, oxymetallations (161) (M = Hg, Tl, and Pb), particularly using heavy metal acetates, and insertion into XMg—N< bonds (230b) are the subject of other papers. In the vast majority of these systems, organometallic compounds are merely transient intermediates.

(3) In Section V, we shall generally exclude those experiments in which the organometallic product was not isolated. That insertions play a key role in such processes is, however, an important step for their proper understanding. In the area of main group chemistry, the principal examples are (i) Grignard-type syntheses (160a) [and related reactions involving other organometallics, especially derivatives of Al, Zn, Cd, and Hg (61b)]; (ii) hydrometallations [hydroboration (42) is of greatest utility in organic research, while hydrometallation with Group IV (Si, Ge, Sn, and Pb) hydrides (177a) is of wider technological value]; (iii) certain Friedel-Crafts-type syntheses (see, for example, Section III, B); and (iv) chain-growth reactions, of which the most important are Ziegler-Natta polymerizations of olefins (164a) [the alkyl growth reaction is also shown (125a) by certain organic derivatives of Li, K, Be, Mg, B, Al, Ga, In, and Ti], and the catalytic (e.g., R₃MOR'; M = Sn or Pb) conversions of isocyanates into cyanurates (29, 79b) or urethanes (25, 79b). In transition metal chemistry, examples of

processes in which insertion reactions probably play a part (19a, 113a, 125a, 215a, 220b) include the catalytic reduction of olefins, the oxidation of olefins to carbonyl compounds, and the synthesis of acrylates from acetylene, carbon monoxide' and hydroxylic solvents.

(4) Hydrometallation reactions, i.e., insertions into the M—H bond are omitted, particularly so since there are recent reviews dealing with hydroboration (42), and reactions of Al—H (164a), Si—H (177a), Ge—H (177a), Sn—H (177a), Pb—H (177a), and transition metal M—H (111c).

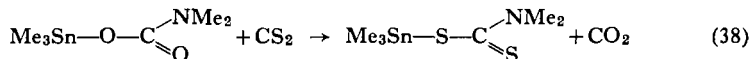
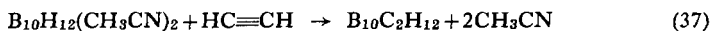
(5) Finally, attention is restricted to insertions of unsaturated substrates, and therefore class (c) is not included. Organometallic nitrenes invariably arise from corresponding azide (and therefore unsaturated) precursors, and it is therefore appropriate to mention that reactions analogous to Eq. (33) are characteristic not only of azidoboranes (222–225a), but of triphenylsilyl (236) and triphenylgermyl azides Me_3MN_3 (M = Si or Ge); a related reaction is that between triiron dodecacarbonyl and phenyl azide to give (II) (181).



The air-oxidation of organometallic compounds of type $\text{MR}_{(n+1)}$ is a feature of their chemistry. It is extremely rare (78), however, that a peroxidic intermediate $\text{R}_n\text{M} - \text{O} - \text{OR}$ [as in Eq. (23)] can be isolated.

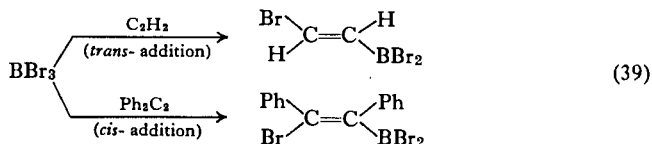
The conversion of nitrogen into ammonia by reagents such as $(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}_2/\text{EtMgCl}$ (276a) may involve insertion of molecular nitrogen into Ti—H bonds (38a).

Not considered are substitution reactions, some of which, however, have a close affinity with insertions as defined by Eqs. (1) and (25). Carborane syntheses [e.g., see Eq. (37) (220a)] and displacement reactions [e.g., see Eq. (38) (95)] are such examples.

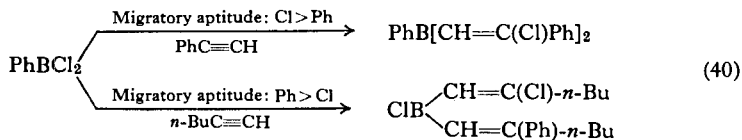


It is to be hoped that more extensive physical studies will become available, especially in relation to kinetics and mechanism [these have been restricted to CO insertions (see Section IV, B) Grignard reactions (277a), and the $\text{PhCN}/\text{AlMe}_3$ system (228a)] and thermochemistry. The latter may be particularly relevant, because there is much circumstantial

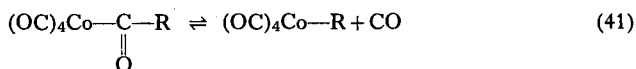
evidence that many of the reactions are low activation energy processes which are thermodynamically rather than kinetically controlled (69, 71, 95, 149, 155b, 158, 167, 168). The main pointers are (i) many of the reactions are fast and occur under very mild conditions (see Section V); (ii) both the direction (see Section V) and stereochemistry [the stereochemistry of alkyne insertions has been reviewed (168); e.g., see Eq. (39) (168)] of addition are frequently governed by stability considerations;



(iii) relative migratory aptitudes of groups X [see Eq. (1)] are often easiest to rationalize in terms of thermochemical criteria [e.g., Eq. (40) (168)];

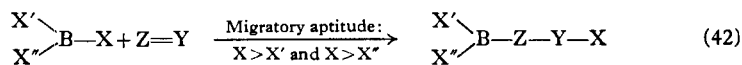


(iv) many of the additions are reversible [e.g., Eq. (41) (125a)] (but in this review we are not otherwise concerned with their retrogressions);



and (v) [a corollary of (iv)] displacement reactions [e.g., Eq. (38) (95)] are known.

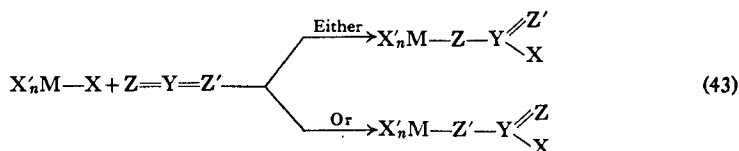
The problem of relative migratory aptitudes of groups X [see Eq. (1)] has been considered in most detail for additions to boron compounds, by means of experiments of the type shown in Eq. (42).



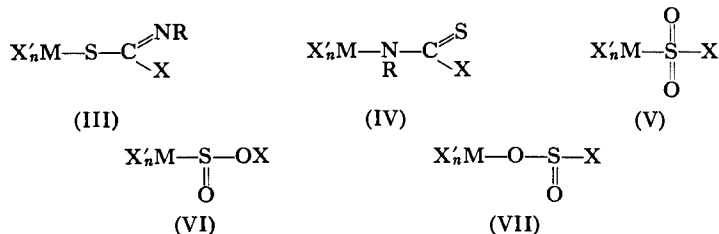
The orders of relative migratory aptitudes of groups X [from $\angle \text{B}-\text{X}$] are (i) $\text{NHR} > \text{NR}_2 > \text{SR} > \text{Ph} > \text{Cl}$; (ii) $\text{OR} > \text{Ph}$; and (iii) $\text{Cl} > \text{OR}$, with respect to insertion of *p*-tolyl carbodiimide (149), and these orders generally [but see, e.g., Eq. (40)] hold for borane additions to other unsaturated substrates. It is probable that migratory aptitude orders are likely to be characteristic for each element. Insertion reactions are facilitated when

weak bonds are broken and stronger bonds are made. For example, it is no accident that in tin(IV) chemistry, $\text{Me}_3\text{SnNMe}_2$ is the most versatile reagent examined to date (more reactive, for example, than Me_3SnOMe); it is a consequence of a very low $\text{Sn}-\text{N}$ bond energy term ($\sim 40 \text{ kcal mole}^{-1}$) (155*b*). More generally, class (b) acceptors are likely to resist insertions involving cleavage of $\text{M}-\text{S}$ or $\text{M}-\text{P}$ bonds when these are to be replaced by $\text{M}-\text{O}$ or $\text{M}-\text{N}$. A complete description of the thermochemistry of insertion requires knowledge [in terms of the bond energy term (\bar{E}) concept] of [see Eq. (1)] $\bar{E}(\text{M}-\text{X})$, $\bar{E}(\text{Z}=\text{Y})$, $\bar{E}(\text{M}-\text{Z})$, $\bar{E}(\text{Z}-\text{Y})$, and $\bar{E}(\text{Y}-\text{X})$.

In addition reactions of unsymmetrical cumulative unsaturated compounds (i.e., RNCO , RNCS , $\text{CH}_2=\text{C}=\text{O}$, OCS , and PhNSO), there is ambiguity about the structures of products, as, for example, in Eq. (43).

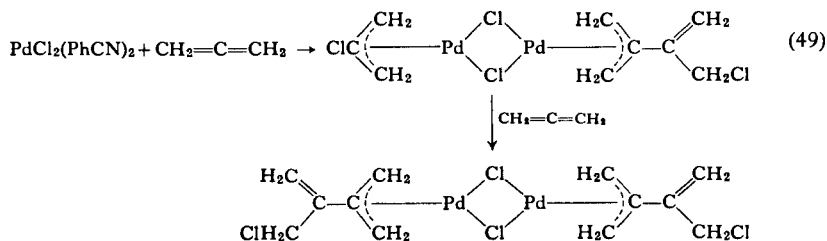
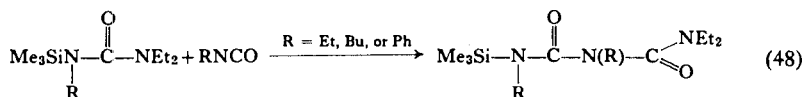
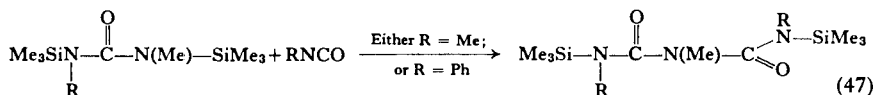
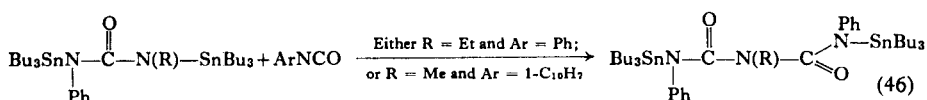
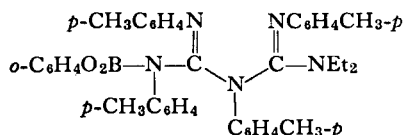
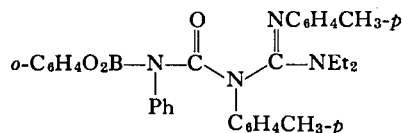


In the Tables, we write addition products of isocyanates, isothiocyanates, ketene, and *N*-thionylaniline (with COS , spectroscopic data are unequivocal) as adducts to $\text{N}=\text{C}$, $\text{N}=\text{C}$, $\text{C}=\text{C}$, and $\text{N}=\text{S}$ bonds [e.g., as (IV)], but this may not invariably be correct. Particularly with isothiocyanates, it is possible that both modes of addition are found under different circumstances, and that (III) is favored over (IV) when M is of pronounced class (b) character. For similar reasons, structure (V) was preferred over (VI) or (VII) for the Mo , Mn , and Fe sulfur dioxide insertion products (see Table IV) (19, 117, 288*a*).



Inspection of Eqs. (1), (25), and (30) will show that the products $\text{X}'_n\text{M}-\text{ZY}-\text{X}$, $\text{X}'_n\text{M}-\text{Z}'(\text{X})\text{Y}'$, and $\text{X}'_n\text{M}-\text{Z}''(\text{Y}'')\text{X}$ are of the same form as the reactants, i.e., M has not changed coordination number. The question

of multiple insertions therefore arises. These have been realized for certain polymerization or oligomerization reactions [see (3) above], but it should be pointed out that a very few two-step insertions [Eqs. (44) and (45) (149); (46) (29a); (47) (163); (48) (87), and (49) (257b)] are also known in which the organometallic product is actually isolated. It seems that the reaction typically stops at the 1:1 stage, at least in part, for reasons of solubility—the 1:1-complex being precipitated from solution.

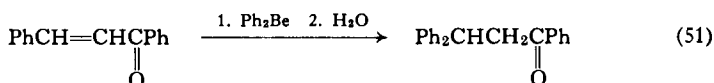
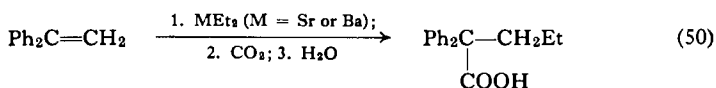


III

1,2-ADDITION OF METAL COMPLEXES TO UNSATURATED SUBSTRATES

A. Insertion Reactions of Alkenes and Alkynes (also 1,4-Addition)

For organic derivatives of *Be*, *Mg*, *Ca*, *Sr*, and *Ba* there are some data which indicate additivity to an olefinic site [Eq. (50) (101a, 108a); and Eq. (51) (106)].



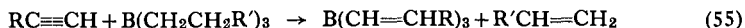
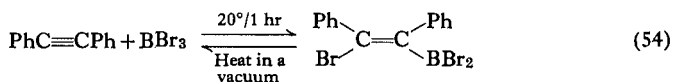
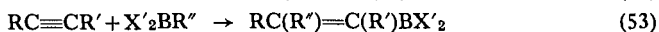
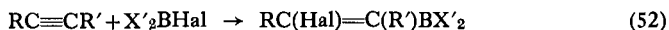
The insertion products were not isolated, but their formation may be inferred from the nature of the hydrolysates. It is relevant that derivatives of the alkaline earth metals are especially reactive (see Section III, G) and that 1,1-diphenylethylene can be responsive (as are conjugated keto alkenes) to nucleophilic attack. By contrast to Eq. (51), PhCaI gave a $\text{C}=\text{O}$ and not a $\text{C}=\text{C}$ adduct (106).

For *boron* compounds (166a), we may recognize four principal types of situations: (i) $\text{X}'_2\text{BX}$ /alkyne (168); (ii) $\text{X}'_2\text{BX}$ /alkene or allene (158); (iii) $\text{X}'_2\text{BX}$ /polyene (158); and (iv) the B_2X_4 /unsaturated hydrocarbon (57–59, 85, 269) systems.

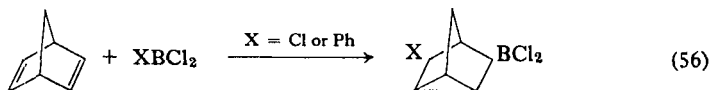
As for (i)–(iii), it is necessary that the borane be a particularly good acceptor (acceptor strengths, generally, decrease in the series $\text{BBr}_3 > \text{BCl}_3 > \text{RBBR}_2 > \text{RBCl}_2 > \text{R}_2\text{BBr} > \text{R}_2\text{BCl}$, where R is alkyl, alkenyl, or aryl) and that the B—X bond be relatively readily cleaved ($\text{B—Br} > \text{B—Cl} > \text{B—C} \gg \text{B—F}$). The high acceptor strength requirement on the borane is less critical for alkynes, which, unlike alkenes, in their more typically organic reactions often favor attack by nucleophiles. In an extreme case [$\text{B}(\text{NMe}_2)_3/\text{EtOOC}\equiv\text{CCOOEt}$], with highly electron-withdrawing groups at the triple bond, it is possible to realize insertion even with the nucleophilic reagent $\text{B}(\text{NMe}_2)_3$ (96).

Reactions of type (iv) may well be free radical in nature, and owe their facility to a weak B—B bond.

The halo- [Eq. (52)] and organo- [Eq. (53)] boronation reactions of alkynes show profound differences with hydroboration in their Markownikoff addition, and their variable steric course (*trans* with C_2H_2 , but *cis* with many substituted acetylenes). Also noteworthy are the increased rate with increase in basicity of the alkyne, the dependence of reactivity on the Lewis acidity of the borane, the variable migratory order [cf. Eq. (39)], and the occasional reversibility [e.g., Eq. (54)]. An alternative reaction path, characteristic of trialkylboranes, is the displacement reaction [Eq. (55)] (166a) [which mechanistically, however, probably also is an insertion reaction, but involving an $HB(CH_2CH_2R')_2$ intermediate (166a)].



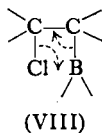
Dienes capable of forming homoallylic cations are prone to undergo addition reactions with haloboranes, as shown, for example, in Eq. (56) (157, 158, 166).



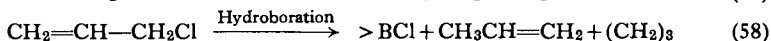
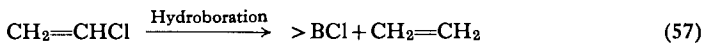
It is interesting that there is not an inevitable correlation between relative migratory orders and rates. Thus, with reference to Eq. (56), whereas $Ph > Cl$ in relative migratory aptitude, relative rates decrease in the series $BCl_3 > PhBCl_2 \gg Ph_2BCl$.

Cycloheptatriene with BCl_3 may yield various products, depending upon reaction conditions (45, 114–117, 157, 158). When the two reagents are heated together, an elimination–rearrangement reaction leads to $PhCH_2BCl_2$ (157, 158), while at ambient temperature without solvent, or in dichloromethane (114–116), or in presence of *tert*-butyl chloride (45), the product is tropenium tetrachloroborate, $C_7H_7^+BCl_4^-$.

Competing processes for chloroboronation of alkenes are cationic polymerization and the facile dechloroboronation (VIII),

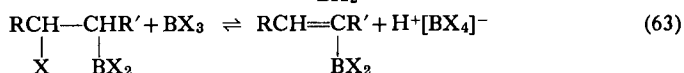
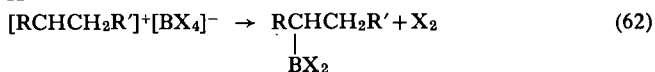
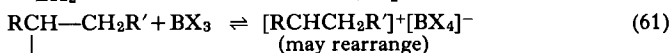
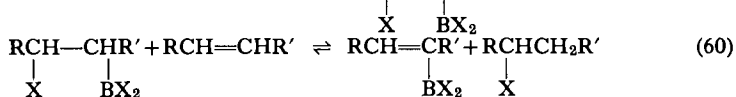
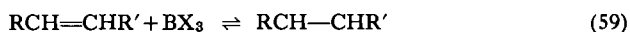


which is characteristic both of chlorovinyllic and chloroallylic systems, as is illustrated by Eqs. (57) and (58).

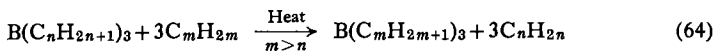


On the other hand, debromoborations are less facile, and the general pattern is for alkenes to yield corresponding alkenyldibromoboranes, alkylidibromoboranes, and bromoalkanes (158).

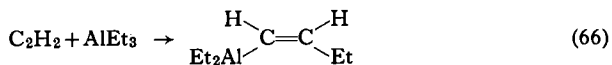
A speculative reaction sequence that accounts for most of the data is shown in Eqs. (59)–(61). An alternative to Eq. (60) may well be Eqs. (62) and (63).



Distillation of trialkylboranes and alkenes normally results not in addition but in displacement [Eq. (64)] (166a). Triethylborane, however, is anomalous in that insertion into a B—C bond is observed (164), as shown in Eq. (65).



Aluminum compounds have been studied very extensively from the standpoint of their reactions with unsaturated hydrocarbons (164a). The main reason for this interest stems from the discovery of the Ziegler catalysts [typically an admixture of $(\text{AlEt}_3)_2/\text{TiCl}_3$] for the polymerization of ethylene under mild conditions, and subsequently Natta's demonstration that α -olefins and 1,3-dienes behave similarly and, moreover, do so stereospecifically, probably with each step involving a cyclic transition state. Triethylalane and acetylene give the *cis* product [Eq. (66)] (285, 286).

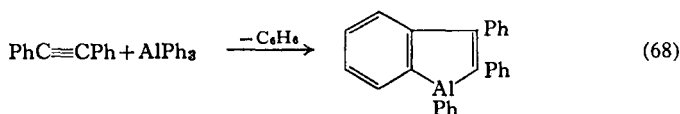
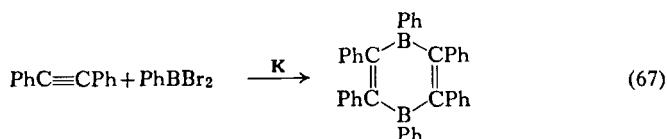


The Al—C bond is rather weak. The presence of bridging Al—C—Al is probably the principal cause of the high susceptibility of the trialkylalanes to undergo the alkene insertion reaction, sometimes to give polymeric materials. In *tert*-Bu₃AlOEt₂, the *tert*-Bu—Al bond is considerably activated compared with the R—Al bond in less-hindered alanes; this has been shown by examination of the comparative reactivities of *tert*-Bu₃AlOEt₂ and Et₃AlOEt₂ with respect to C₂H₄ (171).

The olefin displacement reaction [analogous to Eq. (64)] is a further complication in R₃Al/olefin systems (164a).

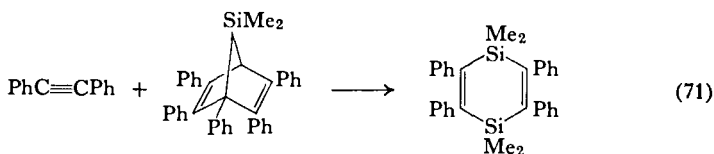
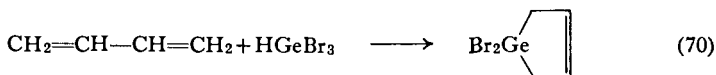
Thallium(III) acetate/unsaturated hydrocarbon reactions probably resemble those of the acetates of mercury(II) and lead(IV) (161).

Both for boron [Eq. (67), the product may actually be an organocarborane] (158) and aluminum [Eq. (68)] (84), we include in Table I examples of reactions which might be considered displacements rather than insertions.



However, in the former, it is likely that a carbene analog of the form PhB: is an intermediate. Similar species may be postulated for certain reactions of *silicon* and *germanium* [and also *titanium* (273)—(π -C₅H₅)₂Ti/PhC≡CPh] derivatives of the form MX₂ (the “silylenes,” for SiX₂). Examples are shown in Eqs. (69) (201, 205); (70) (193); and (71) (100). These reactive intermediates are generated from X₂MCl₂ with Li, Na, or K (98, 99, 202–206, 260, 280); HMCl₃ (\rightleftharpoons HCl + MCl₂) (93b, 191–193, 198, 199); or by pyrolysis of (X₂M)_n (201, 275) or of bridgehead bicyclic compounds such as (IX) (100, 101). It is possible to formulate alternative mechanisms for coupling reactions such as Eq. (69) which do not involve silylene intermediates (279a).



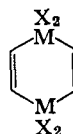


(IX)

The reactions of diphenylacetylene and MX_2 ($\text{M}=\text{Si}$ or Ge) excited particular interest at one time, because of the incorrect (172, 275, 275a) formulation of the products as (X) instead of (XI) (see Table I).

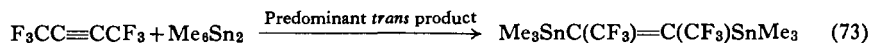
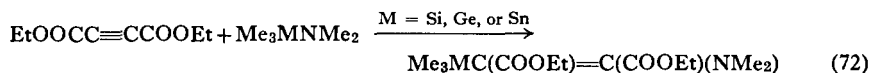


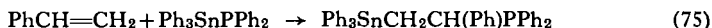
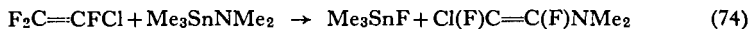
(X)



(XI)

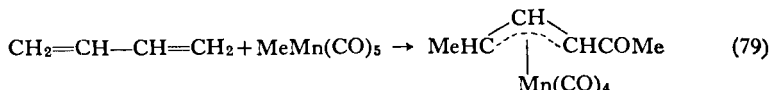
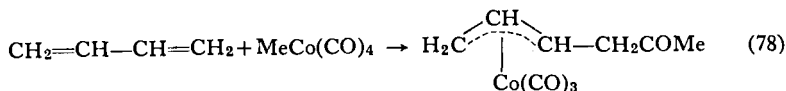
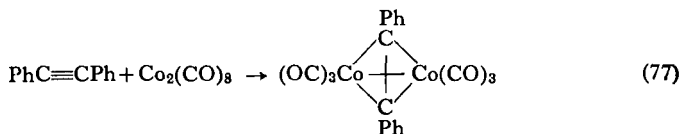
Norbornadiene forms 1:1 adducts with *tin(IV)* chloride or bromide [having a structure similar to that of the product of Eq. (56)], but not with weaker acceptors such as SiCl_4 , GeCl_4 , or MeSnCl_3 (235). An alternative way for tin compounds to be made reactive, and the same applies to their Si and Ge analogs, is by behaving as nucleophiles in their reactions with alkynes having electron-withdrawing substituents [e.g., $\text{R}_3'\text{SnOR}''/\text{ROOCC}\equiv\text{CCOOR}''$ (179) and $\text{Me}_3\text{MnMe}_2/\text{EtOCC}\equiv\text{CCOOEt}$ (96) or $\text{Me}_3\text{SnNMe}_2/\text{PhC}\equiv\text{CCl}$, as in Eq. (72)]. Other examples of $\text{Sn}-\text{C}$ bond-making are shown in the reactions of $\text{Me}_3\text{SnNMe}_2$ with α,β -unsaturated carbonyl and nitrile derivatives, such as $\text{CH}_2=\text{CHCO}_2\text{Me}$ and $\text{CH}_2=\text{CHCN}$ (96). Perfluoroalkenes are likewise susceptible to nucleophilic, rather than electrophilic, attack and therefore a number of examples involving their insertion are found [e.g., Eq. (73) (72)]. However, a complication is a tendency for $\text{Sn}-\text{F}$ bond-making, as in Eq. (74) (96). Finally, organotin compounds may react in a free radical manner [this is also undoubtedly the case for reaction (73)], as in Eq. (75) (259).





Arsenic, antimony, selenium, and tellurium compounds show insertion reactions, either as a result of $\text{M}-\text{Cl}$, $\text{M}-\text{M}$, or $\text{M}-\text{M}'$ cleavage. The halides of these elements behave in many ways as acid halides and it is likely that the $\text{X}_n'\text{M}-\text{Cl}/\text{unsaturated hydrocarbon}$ reactions are similar to the addition reaction of acyl chlorides. In the main, therefore, we visualize a Friedel-Crafts-type mechanism with transient formation of $\text{X}_n'\text{M}^+$, either by using a Lewis acid catalyst, or autocatalytically. Other processes may well be free radical in nature.

In *transition metal chemistry*, particularly prominent are insertion reactions which lead either to π -allyl or σ -polyfluoroalkyl metal complexes. It is certainly no accident that these types of bonding are known to be particularly favorable for stability in organometallic compounds of transition elements. Likewise, $\text{X}_n'\text{M}-\text{X}$ cleavage is particularly characteristic for $\text{M}-\text{R}$, $\text{M}-\text{M}$, and $\text{M}-\text{Cl}$, and the first two are known to be rather weak bonds. Representative examples are shown in Eqs. (76) (282–284); (77) (112a); (78) (123, 124); and (79) (8, 10); (78) and (79) are related, but differ from one another in that in the latter a hydride ion shift must clearly occur. As mentioned in Section II, several important technical processes are likely to involve steps involving alkene or alkyne insertion into transition metal $\text{X}_n'\text{M}-\text{X}$ bonds; this aspect has been reviewed (125a).



Reactions of the type shown in Eq. (77) should strictly not be included, as displacement accompanies insertion.

The rapid polymerization of acrylonitrile, even at -78° , is effected by trace amounts of $\text{Ti(NMe}_2)_4$ (61). This almost certainly involves a multistep

insertion process, which is encouraged by the extreme lability of the Ti—C bond. The alkoxide $\text{Ti}(\text{OPr-iso})_4$ does not react. Methacrylonitrile requires to be refluxed with $\text{Ti}(\text{NMe}_2)_4$ in order for polymerization to set in.

B. Insertion Reactions of Isocyanates, Isothiocyanates, Carbodiimides, Ketene, and Diketene

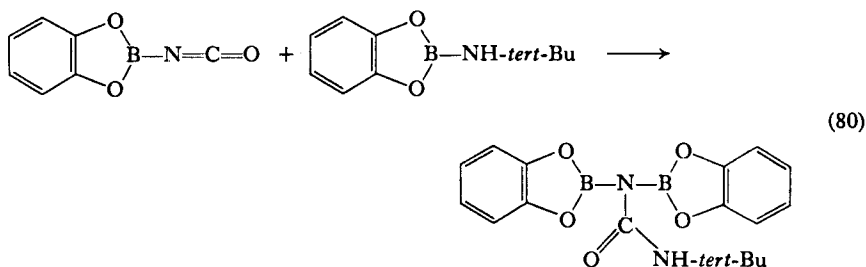
In general, the insertion reactions of metal complexes with isocyanates, isothiocyanates, carbodiimides, and ketene are effected at relatively low temperature and without the use of a catalyst. Yields are essentially quantitative, and it is rare for mixtures of products to be obtained [e.g., compounds of type $\text{Ar}_n\text{B}(\text{Hal})_{3-n}$ (where $n=0, 1, 2$, or 3) form only 1:2 adducts with PhNCO , PhNCS , or $p\text{-CH}_3\text{C}_6\text{H}_4\text{NCNC}_6\text{H}_4\text{CH}_3\text{-}p$ (149, 167), irrespective of the stoichiometry of mixing, whereas $\text{B}(\text{NMe}_2)_3$ cleanly forms 1:1, 1:2, or 1:3 adducts depending on the proportion in which the reagents are mixed (71)].

Insertion reactions of RNCO , RNCS , RNCNR , and CH_2CO into the $\text{X}'_n\text{M—N=}$ bond are the most general (154), and have so far been realized for $\text{M} = \text{B}, \text{Al}, \text{Si}, \text{Ge}, \text{Sn}, \text{P}^{\text{III}}, \text{As}, \text{S}^{\text{IV}}, \text{Ti}^{\text{IV}}, \text{Cr}^{\text{III}}$, and Zn ; there are no examples yet of any aminometallanes being unresponsive to such attack. The reason is probably (for RNCO , RNCS , and RNCNR) that the products of the reactions are also of the form $\text{X}'_n\text{M—N=}$ but, in addition, are stabilized by conjugation with C=O , C=S , or C=N groups. Metal-oxygen cleavage reactions are less facile, but have been demonstrated for $\text{M} = \text{B}, \text{Sn}, \text{Pb}, \text{Sb}^{\text{III}}, \text{Ti}^{\text{IV}}$, and Hg^{II} ; they seem to be more significant when $\text{X}'_n\text{M}^+$ has some (*b*) character, and they are unlikely to be found, for instance, for esters of silicon, $\equiv\text{Si—OR}$. Metal-carbon cleavage reactions have proved to be a feature with compounds having Al—R bonds (it is the bridge bonds which are particularly labile), but are also found with B—aryl (not B—alkyl) and Sb—R derivatives; there should be a good deal of scope for extension, especially into transition metal alkyls and derivatives of Zn , Cd , and Hg , although many M—R bonds ($\text{M} = \text{B}, \text{Si}, \text{Ge}, \text{Sn}$, or As) have been shown to be inert. Other bonds into which insertion of RNCO , RNCS , RNCNR , or CH_2CO is found are M—Hal ($\text{M} = \text{B}$ or Al and $\text{Hal} = \text{Cl}$ or Br), M—P ($\text{M} = \text{Sn}$ or Zn), M—S ($\text{M} = \text{B}$), or M—M ($\text{M} = \text{Fe}^0$), and again we look forward to new developments. The relative ease of cleavage of various M—X bonds can be expressed for a given M in terms of relative migratory aptitude

orders. These have been cited for $M = B$ in Section II. For other elements, data are less complete and may be summarized as follows: (i) in general, $RHN > R_2N \gg$ other values of X (it should be noted that in earlier papers dealing with $X_n'M-NHR$ reagents, it was incorrectly believed that insertion involves the $N-H$ and not the $M-N$ bond); (ii) for $M = Al$, $alkyl > Hal$; (iii) for $M = Sn$ or Hg , $RO > R'$; and (iv) for $M = Zn$, $NR_2 > R'$ and $PR_2 > R'$.

There are indications that, in general, the relative reactivities of the 1,2-dipoles are carbodiimide $>$ isocyanate $>$ isothiocyanate. This may be seen, for example, from the greater thermal stability of ureido- than thio-ureidosilanes with respect to dissociation into their factors, the aminosilanes and isocyanates or isothiocyanates, respectively (163). On the other hand, for $X_n'M^+$ species of pronounced class (b) character, it may well turn out that the isothiocyanates will prove the most effective [see Section II, and structures (III) and (IV)]. As for the structural problem, steric factors may be important also. Thus, triethylalane was supposed to react with $RNCO$ by insertion into the $N=C$ bond unless R was highly hindered ($R = tert-Bu$) when $C=O$ insertion was favored (239); however, this conclusion was inferred from the hydrolysates from complexes which were not isolated (238). As these may, depending on structural features, be dimeric (64a, 142) or chelated monomers (142), the experiment is not too meaningful. There are several other instances of organometallic reagents reacting with isocyanates [$PhCu$ or $PhAg/PhNCO$ (109a)] or ketene [$PhCdBr$, or $PhHgCl$, or Ph_2Hg/CH_2CO (109)], in which insertion may be inferred, although the products were not isolated but hydrolyzed to give amides or ketones, respectively.

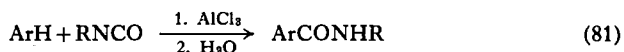
Except for one example [Eq. (80)] (71),



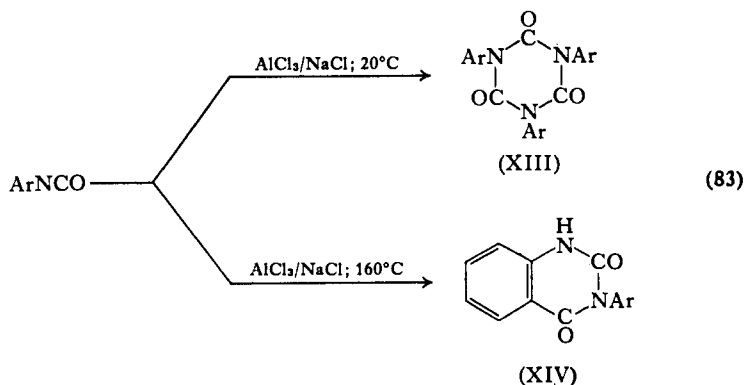
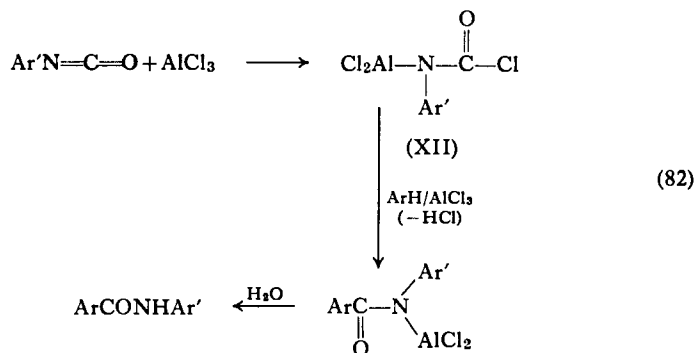
the 1,2-dipoles have invariably been purely organic, and one may look forward to extensions to further organometallic derivatives. However, the

latter may not invariably act as 1,2-dipoles, but may behave as pseudo-halides and give products of metathetical reactions (169a).

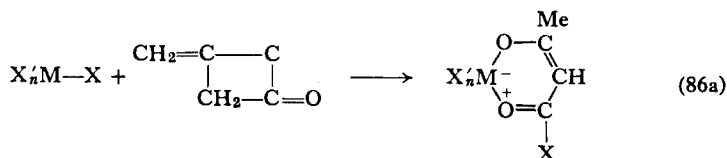
In certain reactions in which aluminum halides are said to behave as Friedel-Crafts catalysts, it seems to us that their catalytic role is better understood in terms of insertion steps. Thus, it was shown that arenes react with isocyanates in the presence of substantial amounts of aluminum chloride to give anilides upon hydrolysis [Eq. (81)] (82a).



An alternative mechanism proposed for such processes, with aryl isocyanates and sulfolane as solvent, involves protonation of the isocyanate (3); this is probably correct for systems in which HBF_4 is the catalyst. An insertion mechanism is proposed in Eq. (82). The first step, the formation of (XII), has been established by an independent experiment (with AlBr_3) (142). The formation of cyanurates (XIII) or the binuclear heterocycles (XIV), as shown in Eq. (83) (80a) is also interpreted to involve insertion reactions



Reactions of diketene are particularly interesting (142) and are generalized in terms of Eq. (86a), in which the product is shown as chelated and O-bonded; monodentate C-bonded products may be formed in some cases.

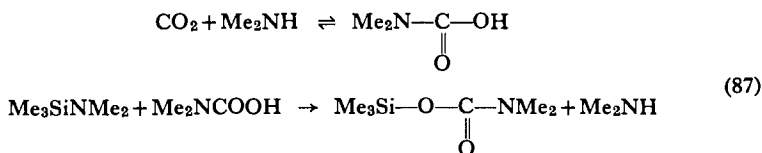


C. Insertion Reactions of Carbon Dioxide, Carbonyl Sulfide, Carbon Disulfide, and N-Thionylamides

Insertion of carbon dioxide into various $X'_nM-N\equiv$ bonds ($M = B, Si, Ge, Sn, P^{III}, As^{III}, S^{IV},$ and T^{IV}), to give organometallic carbamates, has been demonstrated; corresponding insertions of CS_2 (also with $M = Sb^{III}, Zr^{IV}, Nb^V,$ and Ta^V) are also established. Metal-oxygen cleavage has been illustrated for Sn, Ni^{II} (CS_2 only), and Hg^{II} , while examples of insertion into M -alkyl for $Al, M-S$ (CS_2 only for $M = Ni^{II}, Cu^I,$ and Hg^{II}), and $M-P$ (Ph_3SnPPh_2/COS) have been reported. Reactions with X'_nM-Hal and X'_nM-R have failed for $M = B$ or Si (70, 169, 170); *N*-thionylaniline failed to react with aminoboranes (70, 170). As far as the relative ease of cleavage of these various $M-X$ bonds is concerned, similar factors to those discussed in Section III, B are likely to be significant. For example, triethylalane is more reactive than ethylaluminum sesquichloride (238a).

With aminoboranes (70, 170) and aminosilanes (69), carbon dioxide appears to be a more versatile reagent than carbon disulfide. With tin(IV), however, the reverse is true, and may be demonstrated by reference to Eq. (38) (95). This may again be seen as a reflection of the class (*b*) character of tin(IV), and is likely to be a feature also with other of the heavier metals. The greater affinity of tin for sulfur than oxygen is elegantly demonstrated by the experiment with carbonyl sulfide [Eq. (10)].

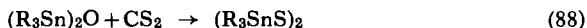
For CX_2 insertions into dimethylaminotrimethylsilane, Me_3SiNMe_2 , a chain mechanism [Eq. (87) for CO_2] was proposed (36, 37).



The evidence was that traces of amines were shown to be necessary, while traces of chlorosilanes (which react with amines) acted as inhibitors. The same feature is found in some related reactions involving B—N and Si—N cleavage (see Table III), but such catalysis is not general [e.g., not in the reactions of $\text{Me}_3\text{SnNMe}_2$ (95)]. The alcohol/sodium hydroxide requirement for CS_2 insertion into RHgOH (164b) may point to a similar mechanism; in the absence of alcohol, the products are RHgSH and COS .

From a comparative study of the carbon disulfide insertion reactions of dimethylamino derivatives of Ti^{IV} , Zr^{IV} , Nb^{V} , and Ta^{V} , it was shown that the expected dithiocarbamatometallanes were obtained, except with $\text{Nb}(\text{NMe}_2)_5$, when the product was $\text{Nb}(\text{SCSNMe}_2)_4$ (35).

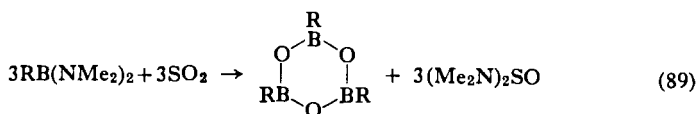
An insertion product may be an intermediate in reaction (88) (236).



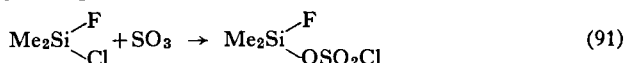
The conversion of Grignard reagents into carboxylic acids by treating them in turn with carbon dioxide and water (or dilute acid) is, of course, very well known (160a). Among other organometallics for which a similar insertion is to be inferred from hydrolysis results are R_3Al (108, 290, 293), R_3In (104), PhTl (105), and Ph_3Tl (105).

D. Insertion Reactions of Sulfur Trioxide, Selenium Trioxide, and Sulfur Dioxide

As in the reactions discussed in Sections III, B and III, C, amino-metallanes are again among the most reactive of metal complexes. However, in the majority of cases, the insertion products are not isolated, due to loss of thionyl or sulfuryl amides with concomitant formation of compounds having $\text{M}=\text{O}$ or $\text{M}-\text{O}-\text{M}$ bonds. This may be illustrated for compounds of *boron* [Eq. (89)] (215) and *titanium* [Eq. (90)] (61); it should be noted that the metal-oxygen products have exceptional thermodynamic stability by virtue of $p\pi-p\pi$ bonding. On the other hand, insertion products have been isolated for derivatives of *silicon* ($\text{Me}_3\text{SiNMe}_2/\text{SO}_3$) (253) and *tin* ($\text{Me}_3\text{SnNMe}_2/\text{SO}_2$) (95).



Complexes of silicon are relatively readily cleaved by oxides of sulfur or selenium, and the reason is at least in part to be found in the exceptionally high Si—O thermochemical bond energy. Thus, unusually for insertion reactions, we even find Si—F (249) and Si—aryl (34, 82) bonds being cleaved (by SO₃). To a lesser extent, this has also been demonstrated for aryl-*germanium* compounds (33). Migratory aptitudes Cl > F are demonstrated by reaction according to Eq. (91) (249).

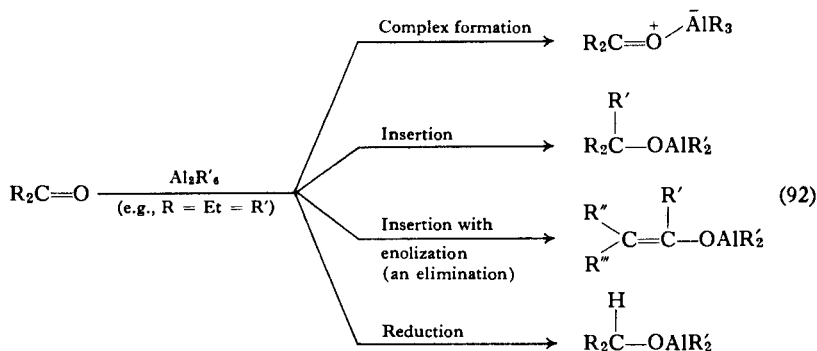


Triethylalane has been converted into the sulfite Al(OSOEt)₃ (6) by means of sulfur dioxide, and similar Al—C cleavage reactions may be inferred from other experiments in which the adducts were not isolated but their hydrolysis afforded sulfinic acids (67, 293).

Sulfur dioxide insertion reactions into transition metal M—R bonds have already been referred to, in connection with the problem of their possible structures (V)–(VII). Cleavage of complexes of Mo^{II}, Mn^I, Fe^{II}, Co^{II}, and Hg^{II} has been effected.

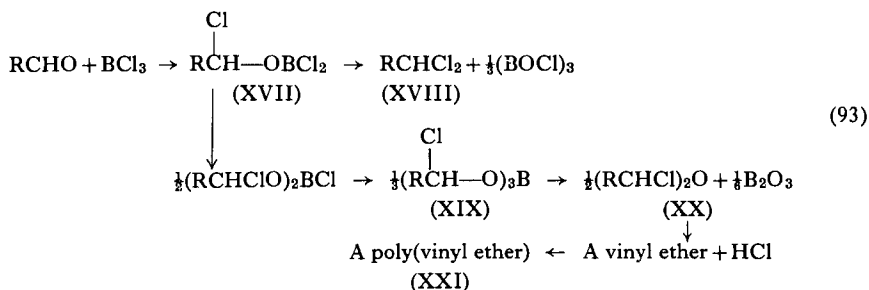
E. Insertion Reactions of Aldehydes and Ketones

With organic carbonyl derivatives [as with other species containing multiply bonded CO, CN, NN, or SO in their functional groups (96a)] we come for the first time to classes of compounds with which metal complexes may yield a multiplicity of products, namely (i) donor–acceptor complexes by virtue of the oxygen (or N) ligand site, (ii) insertion adducts (this may be with enolization), or (iii) products of reduction. This versatility is perhaps most marked for complexes of *aluminum* (49, 93a, 104, 106, 113, 194, 195, 230, 288), and is illustrated by Eq. (92) (230).



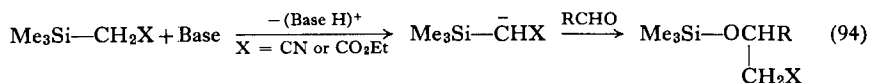
Scheme (92) was proposed from hydrolysis studies of the products. The yield of insertion product increased when an excess of $\text{Al}_2\text{R}'_6$ was used. Triethylalane and $(\text{Et}_2\text{AlCl})_2$ with $\text{iso-Pr}_2\text{CO}$ gave reduction products only, while EtAlCl_2 did not react with $\text{iso-Pr}_2\text{CO}$ below 100°C . It is likely that insertion processes play an essential role in the Tischenko (25, 93a) and Meerwein-Verley-Pondorf (194) reactions, as well as in the Oppenauer oxidation.

Whereas for aluminum complexes, no attempt has yet been made to isolate the organometallic products of carbonyl interaction, with boron derivatives many such species are characterized (see Table V). The most detailed study has been on the BCl_3/RCHO system (90). The proposed generalized reaction sequence is shown in Eq. (93). The nature of the product is a function of R; thus, isolated were (XVII) ($\text{R} = \text{CH}_3\text{CH}=\text{CHCH}_2$ or Ph); (XVIII) [$\text{R} = \text{Ph}$, by heating (XVII)]; (XIX) [$\text{R} = \text{ClCH}_2$, Cl_2CH , CCl_3 , or PhCH_2CH_2]; (XX) ($\text{R} = \text{Me}$, ClCH_2 , *n*-Pr, *iso*-Pr), and (XXI) ($\text{R} = \text{PhCH}_2$); bromal did not react.



That insertion [i.e., to afford (XVII) or (XIX), in terms of Eq. (93)] is encouraged when a group pendant to the carbonyl is electron-withdrawing, such as a polyhaloalkyl, is a feature also found for other borane/carbonyl reactions (see Table V). An example is in the perfluorocyclobutanone series (197, 227). A similar situation is also found in the $\text{RC}\equiv\text{N}/\text{BX}_3$ system (see Section III, G), and for insertion into a *tin* compound [Eq. (16)] (79, 80).

An interesting $\text{X}_n'\text{M}-\text{C}$ cleavage reaction has been reported for a silicon compound (21), as shown in terms of a probable mechanism in Eq. (94).



There is a further complication for metal complex/carbonyl reactions, which is found when the carbonyl compound has α -hydrogen atoms.

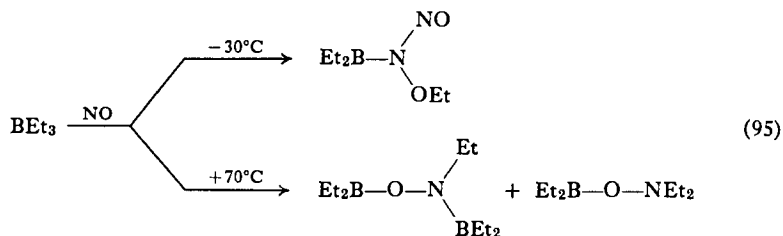
Condensations of the Claisen-Schmidt type are then encountered, and are particularly a feature when the metal complex has pronounced Lewis acid or base character. For example, in the $\text{PhBCl}_2/\text{Me}_2\text{CO}$ (169) or the $\text{Me}_3\text{SnNMe}_2/\text{Me}_2\text{CO}$ systems (155a, 155b), products such as mesityl oxide and phorone have been isolated.

Aldehyde or ketone insertion reactions with organometallic derivatives of B (107), Ga (103), Tl^{I} (105), Tl^{III} (102), and Cu^{I} , as well as the well-known reactions with Grignard reagents (160a), are established, although such products have not been characterized prior to being hydrolyzed.

F. Insertion Reactions of Nitric Oxide, Dinitrogen Tetroxide, Nitrosobenzene, and Nitromethane

Insertion reactions of the type discussed in this section have been restricted to derivatives of *boron*, *aluminum*, and *tin*.

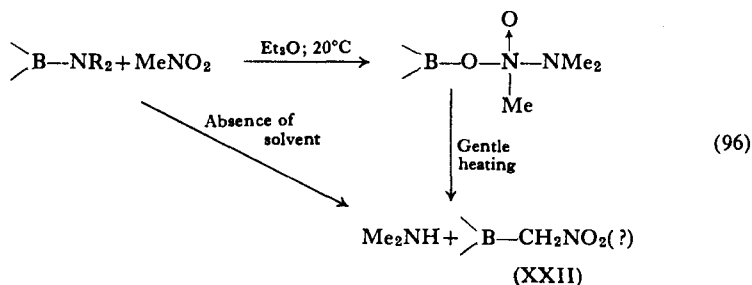
The trialkylborane/nitric oxide system has been examined by several workers (1, 2, 40, 41, 147). The products obtained with triethylborane varied with reaction conditions [Eq. (95)], and it was suggested that the oxide is an ambident nucleophile, changing its active site with temperature.



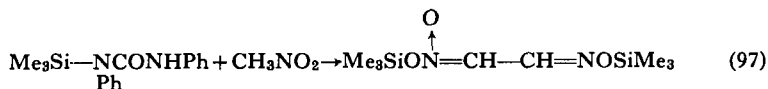
No proposals regarding the structure of the 1:1 adduct of triethylalane and dinitrogen tetroxide have been put forward (6).

The isolation of Bu_2BOH , PhNH_2 , $\text{PhN}(\text{O})\text{NPh}$, and C_4H_8 , after hydrolyzing the residue from nitrosobenzene/tributylborane interaction led to the postulate that this was a 1:1 insertion product (147). This gains credence from an experiment involving $\text{Sn}-\text{N}$ cleavage [Eq. (20)] (96).

Nitromethane adducts have so far only been obtained with amino-boranes (70, 170). The probable course of the reaction, when carried out in ether at 20°C , is shown in the first part of Eq. (96). In the absence of solvent, or by gently heating the adducts, amine elimination was observed and the crystalline products are tentatively supposed to have structure (XXII). A problem with nitromethane, as with cyano and keto



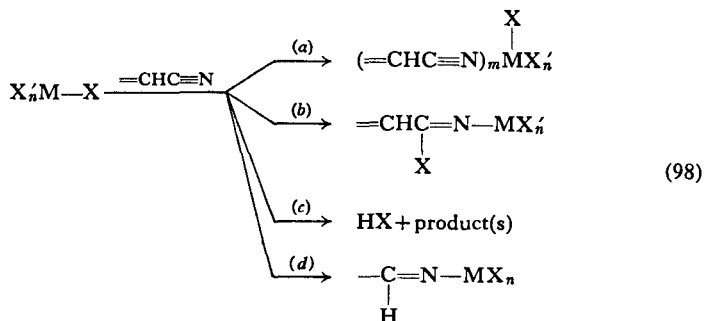
alkanes having α -hydrogen atoms, is its willingness to act also as a protic species. Thus, with $\text{Me}_3\text{SnNMe}_2$, dimethylamine is quantitatively released at 20°C (155a, 155b), and with a $\equiv\text{Si}-\text{N}$ compound at 35°C an elimination process [Eq. (97)] is likewise observed (162a).



With $\text{As}(\text{NMe}_2)_3$, the identified products were As_2O_3 , Me_2NH , and $\text{Me}_2\text{NC}\equiv\text{N}$ (278a).

G. Insertion Reactions of Nitriles

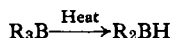
With nitriles, four possible modes of reaction are available [Eq. (98)]. Course (98a) represents donor-acceptor bond formation and is the usual mode of reaction for Lewis acids [unless the $\text{M}-\text{X}$ bond is particularly readily cleaved—see (98b)] and transition metal coordinatively unsaturated



molecules. Course (98b) represents insertion, and it will be seen from Table VII that such reactions have so far been restricted to derivatives of *boron, aluminum, tin, and lead*. On the other hand, it is probably also typical for Grignard reagents (160a) and for organic derivatives of the *alkali metals*

(109b), *Mg*, *Ca* (106a, 109b), *Sr* (109b), and *Ba* (109b), as is evident from their hydrolysis products; a comparative study of relative reactivities showed that these decreased for certain organometallic derivatives in the series $\text{Cs} > \text{Rb} > \text{K} > \text{Na} > \text{Li} > \text{MgBr}$ and $\text{Ba} > \text{Sr} > \text{Ca} > \text{Mg}$ (109b). The greater lability of $\text{Al}-\text{R}$ than $\text{Al}-\text{Cl}$ bonds is once again demonstrated by the lack of reaction between $\text{Et}_3\text{Al}_2\text{Cl}_3$ and certain cyanides, which under similar conditions formed $\text{Et}_3\text{Al} \cdot 2\text{RCN}$ with Al_2Et_6 (238). Reaction (98c) represents the characteristic pattern for $\text{Me}_3\text{Sn}-\text{NMe}_2/\text{MeCN}$ (95, 155, 155a, 155b); aminoboranes do not behave similarly (70, 170). Reaction (94d) represents reduction. The competition between (94b) and (94d) has been studied for the $\text{Et}_3\text{Al}/\text{PhCN}$ system (229a), by hydrolyzing the products to give ethyl phenyl ketone and benzaldehyde (with ethylene), respectively. Using excess of Et_3Al favored (94b), while excess of PhCN encouraged (94d).

The reactions of boron compounds seem to be particularly interesting. Whereas hydroboration of nitriles (98b) proceeds quite smoothly, the boron halides give stable adducts (98a). These dissociate upon heating into their factors rather than rearrange (98b) (96a), or alternatively for $\text{R}_3\text{B} \cdot \text{NCR}'$, give hydroborated species (169) because



On the other hand, CF_3CN has been shown to behave anomalously, reacting according to (98b) with BX_3 ($\text{X} = \text{Cl}$ or Br) (61c). The effect of having a fluorinated side chain is thus similar to that found for carbonyl compounds (see Section III, E). Thioalkylboron compounds readily undergo insertion (188a), doubtless due to the weak $\text{B}-\text{S}$ linkage.

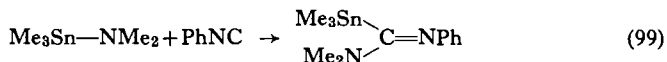
The conversion, by means of organometallic compounds [e.g., R_2Zn (89a), etc. (3a, 150a)], of nitriles into triazines may well prove to proceed by a mechanism involving consecutive insertion processes.

IV

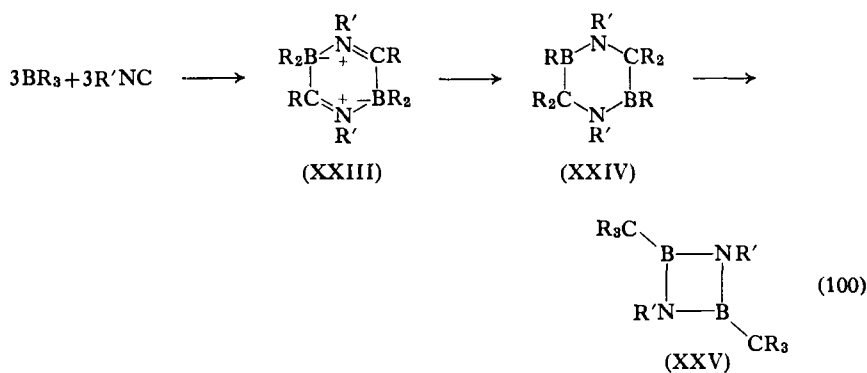
I,1-ADDITION OF METAL COMPLEXES TO UNSATURATED SUBSTRATES

A. Insertion Reactions of Isonitriles

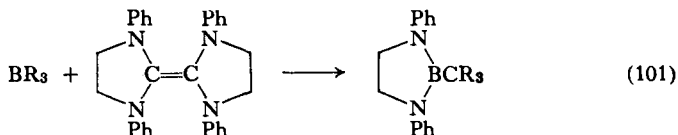
These have not yet been extensively explored (see Table VIII), but examples of *boron*-carbon (38, 55, 56, 131-134) and *tin*-nitrogen [Eq. (99)] (96) bond cleavage have emerged.



This is clearly a particularly fruitful area for further study. Boranes may react with isocyanides to give products of fission of successively one B—C, two B—C, and three B—C bonds as shown in Eq. (100). The complete reaction sequence has been demonstrated for the case of $\text{R} = \text{Et}$ and $\text{R}' = \text{Ph}$ (55); (XXIII) was obtained under mild conditions, and was rearranged into (XXIV) at 200°C , and into (XXV) at 300°C .



A related reaction is shown in Eq. (101) (130).

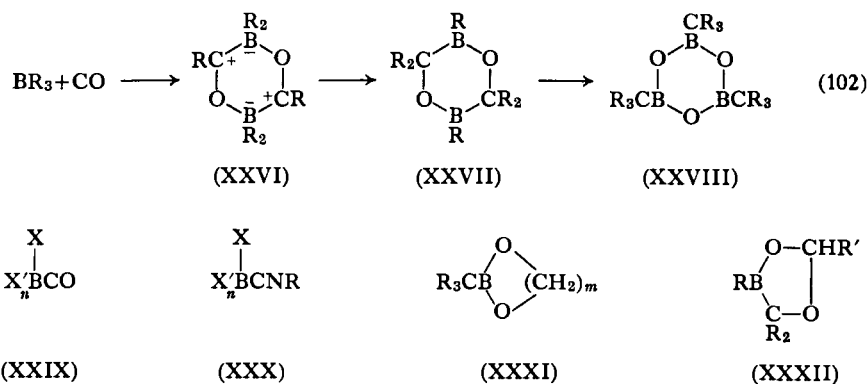


B. Insertion Reactions of Carbon Monoxide

Carbon monoxide insertion reactions which have been observed to date have involved *boron*-carbon or transition metal (*Mo*, *W*, *Mn*, *Fe*, *Co*, *Ni*, *Pd*, or *Pt*)-carbon bond cleavage. There is considerable potential for extensions, and some of the reactions have great catalytic importance (see Section II) (19a, 125a).

The CO insertions into BR_3 resemble the isoelectronic reactions of the isocyanides discussed in Section IV, A. Thus, successive steps in the car-

bonylation are believed to be as shown in Eq. (102), with (XXVI) as a postulated intermediate (138–140); (XXVII) and (XXVIII) have, however, been characterized. In both types of reactions it may be that donor–acceptor complexes (XXIX) and (XXX) are formed initially, but these have only been characterized for $\text{H}_3\text{B} \cdot \text{CO}$ and $\text{B}_4\text{H}_8 \cdot \text{CO}$. The reactions appear to be markedly catalyzed by traces of NaBH_4 (235a). Likewise, whereas the uptake of CO by a THF solution of diborane is negligible at 25° , in presence of a trace of NaBH_4 there is a smooth conversion into $(\text{MeBO})_3$ (235a). The carbonylation of trialkylboranes has been made use of in the synthesis of boronic anhydrides (XXVIII) (139), chelate esters of the type (XXXI) (138), and heterocyclic boron compounds such as (XXXII) (140), by carrying out these reactions in the presence of water, diols, or aldehydes, respectively.



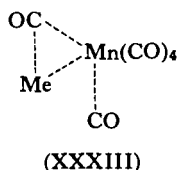
The formation of σ -acyl transition metal derivatives from σ -alkyl compounds, either by treatment with carbon monoxide [e.g., Eq. (27)] (32), or by causing CO to migrate from its position as a free ligand by reaction with a displacing ligand such as an amine, phosphine, arsine, or phosphite [e.g., Eq. (28)] (119a, 127–129) is evidently quite general. For octahedral complexes, it is likely that these are intramolecular processes, as illustrated by Eq. (29) (66). For square-planar complexes, 5-coordinate transition states may be involved (32). This would explain the greater reactivity of palladium over platinum, and in support of the hypothesis, a 5-coordinate cobalt carbonyl $\text{CoX}_2(\text{CO})(\text{PEt}_3)_2$ has been obtained (but not the Ni, Pd, or Pt analogs).

The kinetics of the octahedral insertions has been investigated by two groups of workers (47, 48), (183, 184). The equilibrium and rates

of the forward and reverse reactions in the system illustrated by Eq. (103)



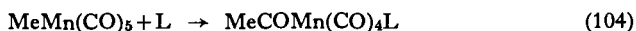
were studied at 1 atm pressure of CO, in various solvents [including $(\text{EtOCH}_2\text{CH}_2)_2\text{O}$], and at various temperatures (47). The reaction was first order in both reactants, the transition state (which is intended to have no geometrical implication) was pictured as (XXXIII), and solvent participation was thought unimportant.



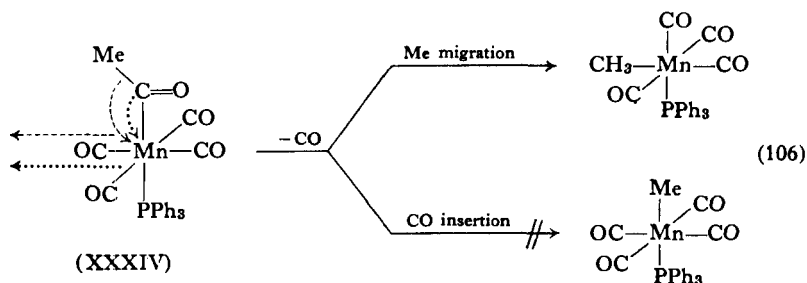
The increase in rate constant with increasing dielectric constant of the medium was taken as evidence that the transition state is more polar than the reactants.

Reaction (104), with $\text{L} = \text{PPh}_3$, was similarly examined (48). The rate was independent of $[\text{PPh}_3]$ and $k_1 = 6.6 \pm 0.5 \times 10^{-4} \text{ sec}^{-1}$ at 30.5°C in $(\text{EtOCH}_2\text{CH}_2)_2\text{O}$. Solvent participation was indicated.

Reaction (104), $\text{L} = \text{C}_6\text{H}_{11}\text{NH}_2$, for amine displacement obeyed a



similar rate law in ethers or nitromethane (183). The product was identified as pure *cis*- $\text{MeCOMn(CO)}_4\text{L}$. In methanol, there was a rate dependence on $[\text{L}]$ [$\text{L} = \text{C}_6\text{H}_{11}\text{NH}_2$, PPh_3 , or P(OPh)_3], while in THF ($\text{L} = \text{C}_6\text{H}_{11}\text{NHMe}$) the reaction did not go to completion. In hexane, the rate was first order in both reactants, while in mesitylene, there was evidence both for a first- and



a second-order path. A unified mechanism involves solvent-assisted dissociation, and only when the coordinating ability of the solvent is low, does L take over its role.

Reaction (105, $L = PPh_3$) was examined in hexane or THF at 25° C (184). The established stereochemistry suggested that the process involves Me migration [--- in (XXXIV)] and not CO insertion [... in (XXXIV)] [Eq. (106)]. Recent work, however, shows that compounds $MeCOMn(CO)_4L$ (including $L = PPh_3$) rapidly equilibrate in solution into *cis* and *trans* isomers (48a, 48b, 48c); if the ligand L is the sterically compact $P(OCH_2)_3CCH_3$, the stereochemical result indicated by Eq. (105) is valid (111b).


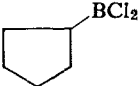

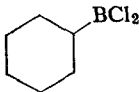
V

TABULAR SURVEY

A survey of the known insertion reactions is presented in Tables I–X. Subject to the limitations outlined in Section II, this survey is complete up to the end of 1965, and some later references are included.

Compounds are arranged according to periodic groups, starting with the boron group. Abbreviations used are Me for methyl, Et for ethyl, Pr for propyl, Bu for butyl, Ph for phenyl, and Ac for acetyl. Because of uncertainty in many cases, aluminum compounds are shown throughout as monomers, although undoubtedly in the majority of cases they are either known to be or will prove to be dimers.

TABLE I
ALKYNE AND ALKENE INSERTION REACTIONS

Reactants		Products	Experimental conditions ^a	References
CH≡CH	BCl ₃	ClCH=CHBCl ₂	Hg ₂ Cl ₂ , charcoal; 5 150°–300°	
PhC≡CH	BCl ₃	ClCH=CHBCl ₂ , (ClCH=CH) ₂ BCl, (ClCH=CH) ₃ B	—	111
CH ₂ =CH ₂	BCl ₃	PhCCl=CHBCl ₂ , (PhCCl=CH) ₂ BCl	–78°	168
		EtBCl ₂ , PrBCl ₂ , BuBCl ₂	Al/AlCl ₃ ; 90°–150°	196
		EtBCl ₂ , CH ₂ =CHBCl ₂	AlCl ₃ or HgCl ₂ ; 100°–300°	287
		EtBCl ₂	H ₂ ; Pt catalyst, ~500°	261
RCH=CH ₂ R = CH ₃ –C ₇ H ₁₅ , and R = BrCH ₂ or BrCH ₂ (CH ₂) ₂	BCl ₃	RCH ₂ CH ₂ BCl ₂	H ₂ ; Pt catalyst, ~500°	261
CH ₃ CH ₂ CH=CH ₂	BCl ₃	EtCHClCH ₂ BCl ₂ , (EtCHClCH ₂) ₂ BCl, (EtCHClCH ₂) ₃ B	SnCl ₂ and peroxide; 20°	94
	BCl ₃		H ₂ ; Pt catalyst, ~500°	261
	BCl ₃		Al/AlCl ₃ ; 90°–150°	196


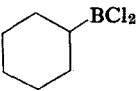

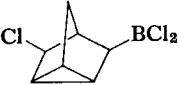

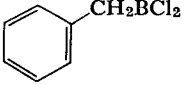
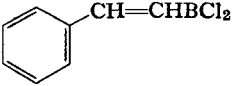

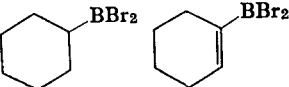
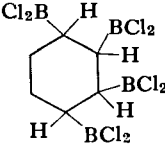
	BCl_3		AlCl_3 or HgCl_2 ; $100^\circ\text{--}300^\circ$	287
	BCl_3		$-78^\circ\text{--}20^\circ$	157, 158, 166
	BCl_3		$60^\circ\text{--}80^\circ$	157, 158
$\text{CH}=\text{CH}$	BBr_3		$-78^\circ\text{--}100^\circ$	158
$\text{PhC}\equiv\text{CPh}$	BBr_3	$\text{CHBr}=\text{CHBBr}_2$, mixture of products	$20^\circ\text{--}25^\circ$ Hg_2Cl_2 ; $150^\circ\text{--}300^\circ$	168 5
$\text{CH}_2=\text{CH}_2$	BBr_3	$\text{PhCBr}=\text{CPhBBr}_2$	20°	168
$\text{RCH}=\text{CH}_2$ $\text{R} = \text{H or } \text{CH}_3\text{--C}_6\text{H}_{13}$	BBr_3	EtBBr_2 , $\text{CH}_2=\text{CHBBr}_2$	AlCl_3 or HgCl_2 ; $100^\circ\text{--}300^\circ$	287
$\text{C}_4\text{H}_9\text{CH}=\text{CH}_2$	BBr_3	$\text{RCH}_2\text{CH}_2\text{BBr}_2$	H_2 ; Pt catalyst; $\sim 500^\circ$	261
$\text{C}_2\text{H}_5\text{CH}=\text{CHC}_2\text{H}_5$	BBr_3	$(\text{C}_4\text{H}_9\text{CHBrCH}_2)_2\text{BBr}$	$95^\circ\text{--}98^\circ$	190
$\text{C}_6\text{H}_{13}\text{CH}=\text{CH}_2$	BBr_3	$(\text{C}_2\text{H}_5\text{CHBrCHC}_2\text{H}_5)_2\text{BBr}$	$95^\circ\text{--}98^\circ$	190
$\text{C}_6\text{H}_{13}\text{CH}=\text{CHCH}_3$	BBr_3	$(\text{C}_6\text{H}_{13}\text{CHBrCH}_2)_2\text{BBr}$	$95^\circ\text{--}98^\circ$	190
		$\text{C}_6\text{H}_{13}\text{CH}_2\text{CH}(\text{BBr}_2)\text{CH}_3$	H_2 ; Pt catalyst; $\sim 500^\circ$	261

TABLE I—continued

260

Reactants	Products	Experimental conditions ^a	References
$(\text{CH}_2)_n \begin{array}{c} \text{CH} \\ \diagup \quad \diagdown \\ \text{CH} \end{array}$ $n = 3, 4$	$(\text{CH}_2)_n \begin{array}{c} \text{CHBBr}_2 \\ \\ \text{CH} \end{array}$	H_2 ; Pt catalyst; $\sim 500^\circ$	261
		$70^\circ\text{--}120^\circ$; or AlCl_3 or HgCl_2 at $100^\circ\text{--}300^\circ$	158, 287
$\text{CH}\equiv\text{CH}$ $\text{CH}_2=\text{CH}_2$ $\text{CH}_3\text{CH}=\text{CHCH}_3$ $\text{CH}=\text{CH}$	$\text{F}_2\text{BCH}=\text{CHBF}_2$ $\text{F}_2\text{BCH}_2\text{CH}_2\text{BF}_2$ $\text{CH}_3\text{CH}(\text{BF}_2)\text{CH}(\text{BF}_2)\text{CH}_3$ $\text{Cl}_2\text{BCH}=\text{CHBCl}_2$ $(\text{Cl}_2\text{B})_2\text{CHCH}(\text{BCl}_2)_2$ $\text{Cl}_2\text{BCH}_2\text{CH}_2\text{BCl}_2$ $\text{CH}_3\text{CH}(\text{BCl}_2)\text{CH}_2\text{BCl}_2$ $\text{CH}_3\text{CH}(\text{BCl}_2)\text{CH}(\text{BCl}_2)\text{CH}_3$ $\text{CH}_2=\text{CHCH}(\text{BCl}_2)\text{CH}_2\text{BCl}_2$ $\text{CH}_2(\text{BCl}_2)\text{CH}(\text{BCl}_2)\text{CH}(\text{BCl}_2)\text{CH}_2\text{BCl}_2$ $\text{C}_2\text{H}_5\text{CH}=\text{CHBCl}(\text{C}_2\text{H}_5)$	140° -23° 90° -45° — -40° -45° -40° $\sim -40^\circ$	57 57 57 57, 58 58, 59 268 57, 85 57 57
$\text{CH}_2=\text{CH}_2$ $\text{CH}_3\text{CH}=\text{CH}_2$ $\text{CH}_3\text{CH}=\text{CHCH}_3$ $\text{CH}_2=\text{CHCH}=\text{CH}_2$	$\text{C}_2\text{H}_5\text{CH}=\text{CHBCl}(\text{C}_2\text{H}_5)$	Charcoal	110
$\text{CH}\equiv\text{CH}$		-80° ; 10 days	291a
$\text{CH}_2=\text{CH}_2$ $\text{C}_8\text{H}_{17}\text{CH}=\text{CH}_2$	$\text{EtCH}_2\text{CH}_2\text{BEt}_2$ $\text{C}_8\text{H}_{17}\text{CH}(\text{Et})\text{CH}_2\text{BEt}_2$	$260^\circ\text{--}280^\circ$ $160^\circ\text{--}170^\circ$	164 164

M. F. LAPPERT and B. PROKAL

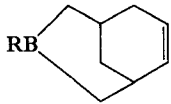

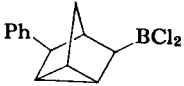
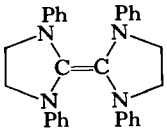
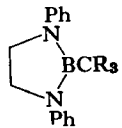
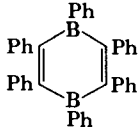

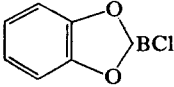
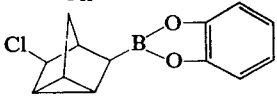
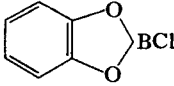
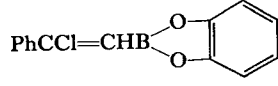
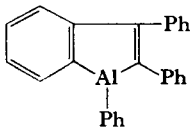

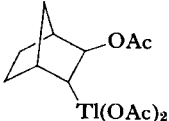
$\text{CH}\equiv\text{CH}$	R_3B $\text{R} = \text{CH}_2 = \text{CH}-\text{CH}_2$		$100^\circ-130^\circ$	188
$\text{C}_4\text{H}_9\text{C}\equiv\text{CH}$	PhBCl_2	$\text{C}_4\text{H}_9\text{C}(\text{Ph})=\text{CH}-\text{BCl}$ $\text{C}_4\text{H}_9\text{C}(\text{Cl})=\text{CH}-$ $(\text{PhCCl}=\text{CH})_2\text{BPh}$	$130^\circ-140^\circ$	168
$\text{PhC}\equiv\text{CH}$	PhBCl_2	$(\text{PhCCl}=\text{CH})_2\text{BPh}$	0°	168
	PhBCl_2		$-78^\circ, -20^\circ$	157, 158
$\text{C}_4\text{H}_9\text{C}\equiv\text{CH}$	Ph_2BCl	$\text{C}_4\text{H}_9\text{C}(\text{Ph})=\text{CHBClPh}$	$130^\circ-140^\circ$	168
	BR_3 $\text{R} = \text{Me}, n\text{-C}_4\text{H}_9, \text{ or } \text{PhCH}_2$		130°	130
$\text{EtOOC}\equiv\text{CCOOEt}$ $\text{PhC}\equiv\text{CPh}$	$\text{B}(\text{NMe}_2)_3$ PhBBr_2	$\text{B}[\text{C}(\text{COOEt})=\text{C}(\text{COOEt})(\text{NMe}_2)]_3$ $\text{PhC}(\text{Br})=\text{CPhBBrPh}$; or	30° 20°	96 83
			$\text{K}; 100^\circ$	158
			100°	157, 158
$\text{PhC}\equiv\text{CH}$			$130^\circ-150^\circ$	168

TABLE I—*continued*

Reactants		Products	Experimental conditions ^a	References
CH ₃ CH=CH ₂	Me ₃ Al	(CH ₃) ₂ CHCH ₂ AlMe ₂	~ 150°	294
(CH ₃) ₂ C=CH ₂	Me ₃ Al	(CH ₃) ₃ CCH ₂ AlMe ₂	~ 200°	231
CH≡CH	Et ₃ Al	EtCH=CHAlEt ₂	40°–60°	285, 286
C ₂ H ₅ C≡CC ₂ H ₅	Et ₃ Al	Et ₂ C=C(Et)AlEt ₂ , Et ₂ C=C(Et)C(Et)=C(Et)AlEt ₂	80°	285
PhC≡CPh	Et ₃ Al	PhC(Et)=CPhAlEt ₂	—	211, 285
CH ₂ =CH ₂	Et ₃ Al	(EtCH ₂ CH ₂) ₃ Al·OEt ₂	Et ₂ O; 60 atm 100°–110°	171
(CH ₃) ₂ C=CH ₂	Et ₃ Al	(CH ₃) ₂ C(Et)CH ₂ AlEt ₂	~ 200°	231
Et ₂ N(CH ₂) _n CH=CH ₂ n = 2, 3	Et ₃ Al	Et ₂ N(CH ₂) _n CH(Et)CH ₂ AlEt ₂	—	291
CH≡CH	iso-Pr ₃ Al	iso-PrCH=CHAl-iso-Pr ₂	140°–160°	286
CH≡CH	iso-Bu ₃ Al	iso-BuCH=CHAl-iso-Bu ₂	—	285
CH ₂ =CH ₂	tert-Bu ₃ Al	tert-(BuCH ₂ CH ₂) ₃ Al·OEt ₂	Et ₂ O; 60 atm	171
PhC≡CPh	Ph ₃ Al		100°–110° 200°	84
CH≡CH	MeC ₅ H ₄ AlEt ₂	Et ₂ AlCH=CHC ₅ H ₄ —Me	25°	165
	Tl(OAc) ₃		25°	226


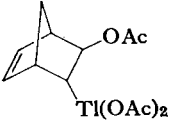
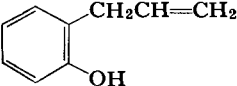
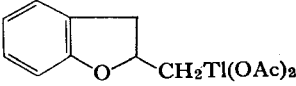

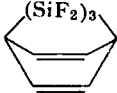
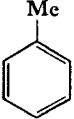
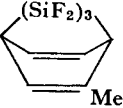

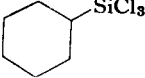
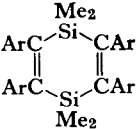
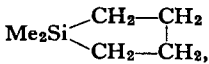
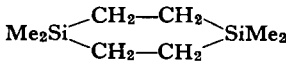
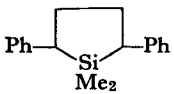
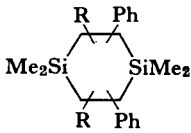
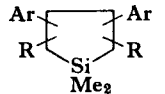
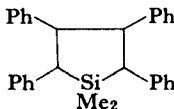
	$\text{Tl}(\text{OAc})_3$		25°	226
$\text{PhCH}=\text{CH}_2$	$\text{Tl}(\text{OAc})_3$	$\text{PhCH}(\text{OMe})\text{CH}_2\text{Tl}(\text{OAc})_2$	0° ; MeOH	159
	$\text{Tl}(\text{OAc})_3$		30° ; AcOH	159
	SiF_2		-196°	265b
	SiF_2		-196°	265b
	SiCl_4		Electron-beam radiation	43
$\text{ArC}\equiv\text{CAr}$ $\text{Ar} = \text{C}_6\text{H}_5, p\text{-CH}_3\text{C}_6\text{H}_4$	Me_2SiCl_2		Na; xylene, $\sim 140^\circ$	152, 153 276, 279

TABLE I—continued

264

M. F. LAPPERT and B. PROKAI

Reactants		Products	Experimental conditions ^a	References
CH ₂ =CH ₂	Me ₂ SiCl ₂		Na; PhH; ~120°	201, 205
			or Li; THF; ~10°	
CH ₂ =CH ₂	Me ₂ SiCl ₂	Me ₂ SiHCH=CH ₂	Na/K; 260°–280°	260
PhCH=CH ₂	Me ₂ SiCl ₂		Li; THF; 10°–70°	99, 202, 203, 280
PhCR=CH ₂ R = H or CH ₃	Me ₂ SiCl ₂		Li; THF; <i>n</i> -C ₇ H ₁₆ ; 20°	206
ArCR=CH ₂ Ar = C ₆ H ₅ ; R = CH ₃ Ar = <i>p</i> -CH ₃ C ₆ H ₄ ; R = H	Me ₂ SiCl ₂		Li; THF; 10°–70°	203
PhCH=CHPh	Me ₂ SiCl ₂		Li; THF; 10°–70°	203, 206

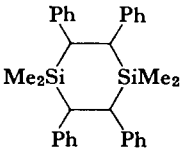
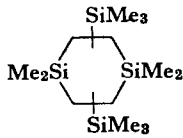
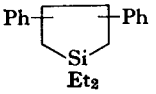

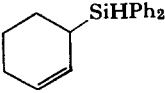
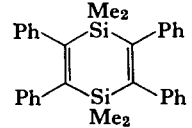
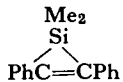
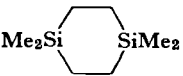
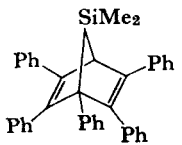
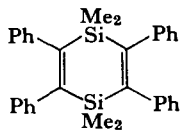
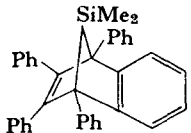
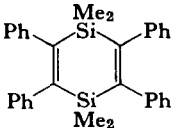
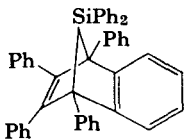
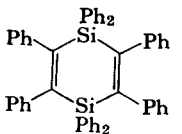

$\text{Me}_3\text{SiCH}=\text{CH}_2$	Me_2SiCl_2		$\text{Li};$ $\text{THF}; n\text{-C}_7\text{H}_{16};$ 20°	206
$\text{EtOOC}\equiv\text{CCOOEt}$	$\text{Me}_3\text{SiNMe}_2$		30°	96
$\text{PhCH}=\text{CH}_2$	Et_2SiCl_2		$\text{Li}; \text{THF};$ $10^\circ\text{--}70^\circ$	206
	Ph_2SiCl_2		$\text{Li}; \text{THF};$ 50° ; trace peroxide	98
$\text{PhC}\equiv\text{CPh}$	$[\text{Me}_2\text{Si}]_n$	 <p>originally believed to be</p> 	140°	275

TABLE I—continued

Reactants		Products	Experimental conditions ^a	References
$\text{CH}_2=\text{CH}_2$	$[\text{Me}_2\text{Si}]_n$	$\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ \diagup \quad \diagdown \\ \text{Me}_2\text{Si} \quad \text{CH}_2-\text{CH}_2 \end{array},$ 	300°	201
$\text{PhC}\equiv\text{CPh}$			300°	100
$\text{PhC}\equiv\text{CPh}$			300°	100
$\text{PhC}\equiv\text{CPh}$			300°	101
$\text{CH}\equiv\text{CH}$	GeCl_2		$\sim 200^\circ$	276, 277

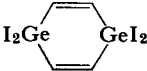
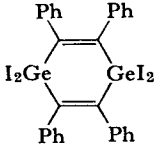
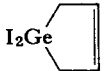
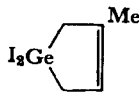
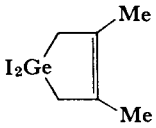
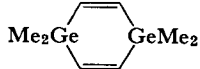
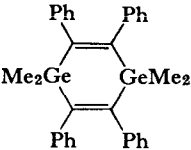
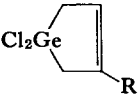
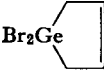
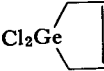
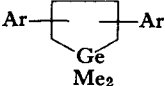
CH=CH CH=CH	GeBr HGeBr ₃	$\text{[-CH=CHGeBr}_2\text{]}_n$ Br ₃ GeCH=CHGeBr ₃ , Br ₃ GeCH ₂ CH ₂ GeBr ₃	—	93b 93b
CH≡CH	GeI ₂		130°–140°	152, 153, 172, 274, 276
PhC≡CPh	GeI ₂		130°–140°	152, 276
CH ₂ =CHCH=CH ₂	GeI ₂		—	182
CH=C(Me)CH=CH ₂	GeI		60°	185a
CH ₂ =C(Me)C(Me)=CH ₂	GeI ₂		—	182, 185a
CH≡CH	GeMe ₂		130°–140°	152, 153, 277

TABLE I—continued

Reactants		Products	Experimental conditions ^a	References
PhC≡CPh	GeMe ₂		130°–140°	152, 153, 277
EtOOC≡CCOOEt	Me ₃ GeNMe ₂	Me ₃ Ge[C(COOEt)≡C(COOEt)(NMe ₂)]	30°	96
CH ₂ =CRCH=CH ₂ R=H, CH ₃	HGeCl ₃		~60°; also -55°	191, 192, 199
CH ₂ =CHCH=CH ₂	HGeBr ₃	 , MeCH=CHCH ₂ GeBr ₃	20°	93b, 193
CH≡CH	Cl ₃ HGe, Et ₂ O	Cl ₂ HGeCH=CHGeCl ₃ , Cl ₃ GeCH=CHGeCl ₃ , -[CH=CHGeCl ₂] _n	20°	198, 200
CH ₂ =CH ₂	Cl ₃ HGe, Et ₂ O	Cl ₂ HGeCH ₂ CH ₂ GeCl ₃ , Cl ₃ GeCH ₂ CH ₂ GeCl ₃ , -[CH ₂ CH ₂ GeCl ₂] _n	20°	198, 200
CH ₂ =CH ₂	Br ₃ HGe	EtGeBr ₃ , Br ₃ GeCH=CH ₂ , Br ₃ GeCH ₂ CH ₂ GeBr ₃	—	93b
CH ₂ =CHCH=CH ₂	Cl ₃ HGe, Et ₂ O	 -[CH ₂ CH=CHCH ₂ GeCl ₂] _n	—	200
ArCH=CH ₂ Ar=C ₆ H ₅ , <i>p</i> -CH ₃ C ₆ H ₄	Me ₂ GeCl ₂		Li; THF; 5°	204


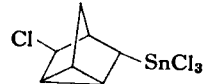

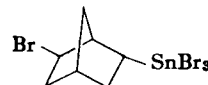

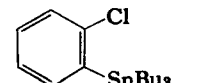
	SnCl_4		0°	235
	SnBr_4		0°	235
	Bu_3SnCl		-70°	267
$\text{EtOOC}\equiv\text{CCOOEt}$	$\text{Me}_3\text{SnNMe}_2$	$\text{EtOOC}-\text{C}(\text{NMe}_2)\text{COOEt}$ SnMe_3	25°	96
$\text{PhC}\equiv\text{CCl}$	$\text{Me}_3\text{SnNMe}_2$	$\text{PhC}=\text{C}(\text{NMe}_2)\text{Cl}$ SnMe_3	25°	96
$\text{PhCH}=\text{CH}_2$	$\text{Ph}_3\text{SnPPh}_2$	$\text{Ph}_3\text{SnCH}_2\text{CH}(\text{Ph})\text{PPh}_2$	—	259
$\text{CH}_2=\text{CHCH}_2\text{Cl}$	$\text{Ph}_3\text{SnPPh}_2$	$\text{Ph}_3\text{SnCH}_2\text{CH}(\text{CH}_2\text{Cl})\text{PPh}_2$	—	259
$\text{PhC}\equiv\text{CH}$	$\text{Ph}_3\text{SnPPh}_2$	$\text{Ph}_3\text{SnCH}=\text{C}(\text{Ph})\text{PPh}_2$	—	259
$\text{CH}_2=\text{CHCO}_2\text{Me}$	$\text{Me}_3\text{SnNMe}_2$	$\text{Me}_3\text{SnCH}-\text{CH}_2\text{NMe}_2$ CO_2Me	25°	96
$\text{CH}_2=\text{C}(\text{Me})\text{CO}_2\text{Me}$	$\text{Me}_3\text{SnNMe}_2$	$\text{CH}_2=\text{C}(\text{Me})\text{CONMe}_2$ + Me_3SnOMe	25°	96
$\text{MeCH}=\text{CHCHO}$	$\text{Me}_3\text{SnNMe}_2$	$\text{Me}_3\text{SnCH}-\text{CH}(\text{Me})\text{NMe}_2$ CHO	25°	96
$\text{CH}_2=\text{CHCN}$	$\text{Me}_3\text{SnNMe}_2$	$\text{Me}_3\text{SnCH}-\text{CH}_2\text{NMe}_2$ CN	25°	96

TABLE I—*continued*

Reactants		Products	Experimental conditions ^a	References
$\text{CH}_2=\text{C}(\text{Me})\text{CN}$	$\text{Me}_3\text{SnNMe}_2$	$\text{Me}_3\text{SnC}(\text{Me})-\text{CH}_2\text{NMe}_2$	25°	96
$\text{CH}_2=\text{CHCN}$	$\text{Sn}(\text{NMe}_2)_4$	$\begin{array}{c} \text{CN} \\ \\ \text{Sn}(\text{CHCH}_2\text{NMe}_2)_4 \\ \\ \text{CN} \end{array}$	25°	61a
$\text{CF}_2=\text{CF}_2$	Ph_2Sn	$\text{Ph}_2\text{SnC}_2\text{F}_4$	UV	12
$\text{CF}_3\text{C}=\text{CCF}_3$	Me_6Sn_2	$\text{Me}_3\text{SnC}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{SnMe}_3$	UV; 100°	72
$\text{CF}_2=\text{CF}_2$	Me_6Sn_2	$\text{Me}_3\text{Sn}(\text{CF}_2\text{CF}_2)_n\text{SnMe}_3$	UV	62, 72
$\text{CF}_3\text{C}=\text{CCF}_3$	Bu_6Sn_2	$\text{Bu}_2\text{Sn}[\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H}]_2$	UV	72
$\text{ROOCC}=\text{CCOOR}$ R = Me, Et	$\text{R}_3'\text{SnOR}'$ R' = Et, Pr, π -Bu R' = Me, Et, Pr	$\begin{array}{c} \text{RO}_2\text{CC}=\text{CCOOR} \\ \quad \\ \text{R}_3'\text{Sn} \quad \text{OR}' \end{array}$	~100°	179
$\text{CF}_2=\text{CFH}$	$\text{Me}_3\text{SnMn}(\text{CO})_5$	$\text{Me}_3\text{SnCF}_2\text{CFHMn}(\text{CO})_5$	UV; 65°	64
$\text{CF}_2=\text{CF}_2$	$\text{Me}_3\text{SnMn}(\text{CO})_5$	$\text{Me}_3\text{SnCF}_2\text{CF}_2\text{Mn}(\text{CO})_5$	UV; 50°	63
$\text{CH}=\text{CH}$	AsCl_3	$\text{ClCH}=\text{CHAsCl}_2$ $(\text{ClCH}=\text{CH})_2\text{AsCl}$ $(\text{ClCH}=\text{CH})_3\text{As}$	AlCl_3 or AlBr_3 or HgCl_2 or Cu_2Cl_2 catalyst; 0°–70°	4, 74, 112, 135, 136, 156, 173, 174, 180, 234, 281
$\text{CH}_2=\text{CH}_2$	AsCl_3	$\text{ClCH}_2\text{CH}_2\text{AsCl}_2$	AlCl_3 catalyst	208, 240,
$\text{CF}_2=\text{CF}_2$	AsCl_3	$\text{Cl}_2\text{AsCF}_2\text{CF}_3$	—	44
$\text{CH}=\text{CH}$	AsBr_3	$\text{BrCH}=\text{CHAsBr}_2$ $(\text{BrCH}=\text{CH})_2\text{AsBr}$ $(\text{BrCH}=\text{CH})_3\text{As}$	AlCl_3 catalyst; ~40°	174, 250

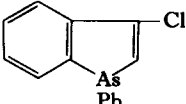
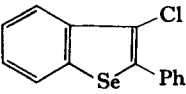

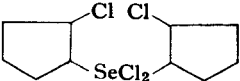

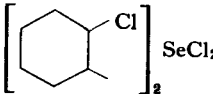
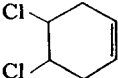
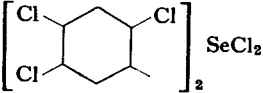
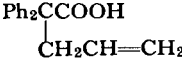
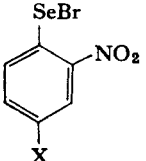
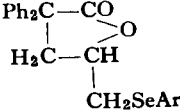
$\text{CH}\equiv\text{CH}$	MeAsCl_2	$\text{ClCH}=\text{CHAsClMe}$, $(\text{ClCH}=\text{CH})_2\text{AsMe}$	AlCl_3 catalyst; $\sim 20^\circ$	75
$\text{CF}_3\text{C}\equiv\text{CCF}_3$	Me_2AsCl	$\text{Me}_2\text{AsC}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{Cl}$	UV	72
$\text{CH}\equiv\text{CH}$	PhAsCl_2	$\text{ClCH}=\text{CHAsClPh}$, $(\text{ClCH}=\text{CH})_2\text{AsPh}$, $\text{ClCH}=\text{CHAsPh}_2$	AlCl_3 catalyst; $\sim 0^\circ$	7, 76, 145
$\text{PhC}\equiv\text{CH}$	PhAsCl_2		$140^\circ\text{--}150^\circ$	77
$\text{CF}_3\text{C}\equiv\text{CCF}_2$	Me_4As_2	$\text{Me}_2\text{AsC}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{AsMe}_2$	20°	73
$\text{CF}_2=\text{CF}_2$	Me_4As_2	$\text{Me}_2\text{As}(\text{CF}_2\text{CF}_2)_4\text{AsMe}_2$	UV; 20°	73
$\text{CBrF}=\text{CF}_2$	Me_4As_2	$\text{Me}_2\text{AsCFBrCF}_2\text{AsMe}_2$	50°	73
$\text{CF}_3\text{CF}=\text{CF}_2$	Me_4As_2	$\text{Me}_2\text{AsCF}(\text{CF}_3)\text{CF}_2\text{AsMe}_2$	50°	73
$\begin{array}{c} \text{CF}_2-\text{CF} \\ \quad \quad \\ \text{CF}_2-\text{CF} \end{array}$	Me_4As_2	$\begin{array}{c} \text{CF}_2-\text{CF} \\ \quad \quad \\ \text{CF}_2-\text{C}-\text{AsMe}_2, \\ \text{FAsMe}_2 \end{array}$	20°	73
$\text{CH}\equiv\text{CH}$	SbCl_5	$(\text{ClCH}=\text{CH})_3\text{SbCl}_2$ $(\text{ClCH}=\text{CH})_2\text{SbCl}_3$	HgCl_2 catalyst; KOH; 50°	14-16, 110, 209, 210, 262
$\text{CH}_2=\text{CH}_2$	Se_2Cl_2	$(\text{CH}_2\text{ClCH}_2)_2\text{SeCl}_2$	$\sim 60^\circ$	11
$\text{RCH}=\text{CH}_2$ R = Me, Et	Se_2Cl_2	$(\text{RCHClCH}_2)_2\text{Se}$, $(\text{RCHClCH}_2)_2\text{SeCl}_2$	$\sim 60^\circ$	31
$\text{CH}\equiv\text{CH}$	SeCl_4	$(\text{CHCl}=\text{CH})_2\text{SeCl}_2$	$\sim 40^\circ$	242, 243
$\text{PhC}\equiv\text{CH}$	SeCl_4	$(\text{PhCCl}=\text{CH})_2\text{SeCl}_2$	25°	243
$\text{PhC}\equiv\text{CPh}$	SeCl_4		—	244
$\text{RCH}=\text{CH}_2$ R = H, Me, Cl, CH_2Cl , C_4H_9 , Ph, CN	SeCl_4	$(\text{RCHClCH}_2)_2\text{SeCl}_2$, $(\text{RCHClCH}_2)_2\text{Se}$	$\sim 25^\circ$	39, 93, 243, 245 93, 245

TABLE I—continued

Reactants	Products	Experimental conditions ^a	References
	SeCl ₄		-78° 243
	SeCl ₄		-78° 243
	SeCl ₄		-78° 243
RCH=CH ₂ R = H, CH ₂ Br	SeBr ₄	(RCHBrCH ₂) ₂ SeBr ₂	~0° 13, 93, 245
RCH=CH ₂ R = H, Me, Et, Pr, Cl	SeOCl ₂	(RCHClCH ₂) ₂ SeCl ₂ , SeO ₂	25° 91
	 X = NO ₂ , Br, Me		~50° 50

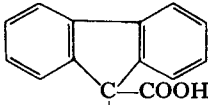

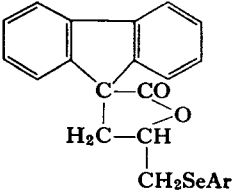

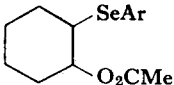

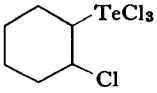

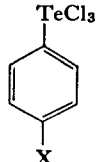
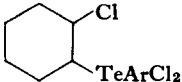
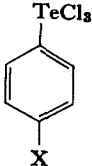
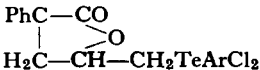

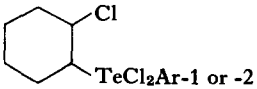
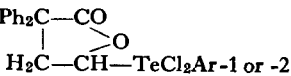
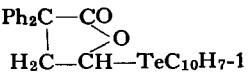
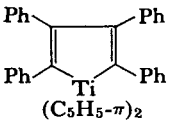
 RCH=CH_2 $\text{R} = \text{H, Me, Ph, OCOMe}$	 $\text{X} = \text{NO}_2, \text{Br, Me}$ $\text{ArSeO}_2\text{CMe}^b$	 $\text{RSeCRHCH}_2\text{O}_2\text{CMe}$	~ 50°	50
 $\text{PhC}\equiv\text{CH}$ $\text{PhC}\equiv\text{CPh}$	$\text{ArSeO}_2\text{CMe}^b$ TeCl_4 TeCl_4	 PhCCl=CHTeCl_3 PhCCl=CPhTeCl_3	~ 100° — 25° ~ 60°	141 141, 151 53 53
 $\text{Ph}_2\text{C-COOH}$ $\text{CH}_2\text{CH=CH}_2$	TeCl_4 TeCl_4	 $\text{Ph}_2\text{C-CO}$ $\text{H}_2\text{C-CH-CH}_2\text{TeCl}_3$	~ 80° ~ 50°	51 52
	 $\text{X} = \text{H, OEt, OPh}$		80°	51, 52

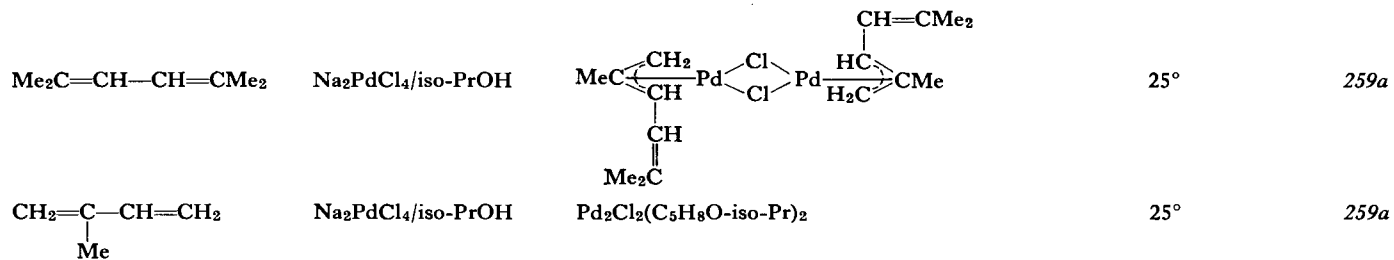
TABLE I—continued

Reactants	Products	Experimental conditions ^a	References
$\text{Ph}_2\text{C}-\text{COOH}$ $\text{CH}_2\text{CH}=\text{CH}_2$	 $\text{X} = \text{H, OEt, OPh}$	 60°	50, 52
	1- and 2- $\text{C}_{10}\text{H}_7\text{TeCl}_3$	 $\sim 80^\circ$	52
$\text{Ph}_2\text{C}-\text{COOH}$ $\text{CH}_2\text{CH}=\text{CH}_2$	1- and 2- $\text{C}_{10}\text{H}_7\text{TeCl}_3$	 $\sim 60^\circ$	50, 52
$\text{Ph}_2\text{C}-\text{COOH}$ $\text{CH}_2\text{CH}=\text{CH}_2$	1- $\text{C}_{10}\text{H}_7\text{TeI}$	 $\sim 80^\circ$	50
$\text{PhC}\equiv\text{CPh}$	$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}$	 60°	273
$\text{CF}_2=\text{CF}_2$	$\text{MeMn}(\text{CO})_5$	$\text{MeCF}_2\text{CF}_2\text{Mn}(\text{CO})_5$	90°, 1–2 atm or 282–284
$\text{CClF}=\text{CF}_2$	$\text{MeMn}(\text{CO})_5$	$\text{MeCF}_2\text{CFClMn}(\text{CO})_5$	UV, 1–2 atm 282–284

$\text{CF}_2=\text{CF}_2$	PhMn(CO)_5	$\text{PhCF}_2\text{CF}_2\text{Mn(CO)}_5$	100°	283, 284
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	RMn(CO)_5 $\text{R} = \text{Me or Ph}$	$\begin{array}{c} \text{H} \\ \\ \text{MeHC} - \text{C} = \text{CHCOR} \\ \\ \text{Mn(CO)}_4 \end{array}$	20° , 21 days	8, 10
$\text{CF}_2=\text{CF}_2$	$\text{Me}_3\text{SnMn(CO)}_5$	$\text{Me}_3\text{SnCF}_2\text{CF}_2\text{Mn(CO)}_5$	—	62
$\text{CF}_2=\text{CF}_2$	MeRe(CO)_5	$\text{MeCF}_2\text{CF}_2\text{Re(CO)}_5$, $\text{Me(CF}_2)_4\text{Re(CO)}_5$	130° , 20 atm	282
$\text{CF}_2=\text{CF}_2$	$\text{Co}_2(\text{CO})_8$	$(\text{CO})_4\text{CoCF}_2\text{CF}_2\text{Co(CO)}_4$	—	278
$\text{R}^1\text{R}^2\text{C}=\text{CR}^3-\text{CR}^4=\text{CR}^5\text{R}^6$ e.g., C_4H_6	MeCo(CO)_4	$\begin{array}{c} \text{R}^3 \\ \\ \text{R}^1 - \text{C} = \text{C} - \text{R}^4 \quad \text{R}^5 \\ \quad \quad \\ \text{R}^2 \quad \quad \text{Co(CO)}_3 - \text{C} - \text{R}^6 - \text{COMe} \end{array}$	0°	123, 124
$\text{R}^1\text{R}^2\text{C}=\text{CR}^3-\text{CR}^4=\text{CR}^5\text{R}^6$ e.g., C_4H_6	MeCOCOC(CO)_4	$\begin{array}{c} \text{R}^3 \\ \\ \text{R}^1 - \text{C} = \text{C} - \text{R}^4 \quad \text{R}^5 \\ \quad \quad \\ \text{R}^2 \quad \quad \text{Co(CO)}_3 - \text{C} - \text{R}^6 - \text{COMe} \end{array}$	0°	123, 124
$\text{RC}\equiv\text{CR}'$ e.g., $\text{R} = \text{Ph} = \text{R}'$	$\text{Co}_2(\text{CO})_8$	$\begin{array}{c} \text{R} \\ \\ (\text{CO})_3\text{Co} - \text{C} - \text{Co(CO)}_3 \\ \\ \text{R}' \end{array}$	20°	112a
$\text{HC}\equiv\text{CH}$	$\text{K}_6[\text{Co(CN)}_5]_2$	$\text{K}_6[(\text{NC})_5\text{CoCH}=\text{CHCo(CN)}_5]$	—	112b
$\text{RC}\equiv\text{CR}'$ $\text{R} = \text{Ph} = \text{R}'$; $\text{R} = \text{Ph}$, $\text{R}' = \text{H}$; $\text{R} = \text{C}_4\text{H}_9$, $\text{R} = \text{H}$	$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \pi\text{-C}_5\text{H}_5\text{Ni} \quad \text{NiC}_5\text{H}_5\text{-}\pi \\ \diagdown \quad \diagup \\ \text{O} \end{array}$	$\begin{array}{c} \text{R} \\ \\ \pi\text{-C}_5\text{H}_5\text{Ni} - \text{C} - \text{NiC}_5\text{H}_5\text{-}\pi \\ \\ \text{R}' \end{array}$	—	265a
$\text{CH}_2=\text{C}=\text{CH}_2$	$\text{PdCl}_2(\text{PhCN})_2$	$\begin{array}{c} \text{CH}_2 \quad \text{Cl} \quad \text{H}_2\text{C} \\ \diagup \quad \diagdown \quad \diagup \quad \diagdown \\ \text{ClC} \quad \text{Pd} \quad \text{Pd} \quad \text{CCl} \\ \diagdown \quad \diagup \quad \diagdown \quad \diagup \\ \text{CH}_2 \quad \text{Cl} \quad \text{H}_2\text{C} \end{array}$	25° in C_6H_6	177b, 257a

TABLE I—continued

Reactants		Products	Experimental conditions ^a	References
		$\text{ClC} \begin{array}{c} \text{CH}_2 \\ \text{CH}_2 \end{array} \text{Pd} \begin{array}{c} \text{Cl} \\ \text{Cl} \end{array} \text{Pd} \begin{array}{c} \text{H}_2\text{C} \\ \text{H}_2\text{C} \end{array} \text{C} \begin{array}{c} \text{CH}_2 \\ \text{CH}_2\text{Cl} \end{array}$	—	257b
		$\text{H}_2\text{C} \begin{array}{c} \text{CH}_2 \\ \text{CH}_2\text{C} \end{array} \text{C} \begin{array}{c} \text{CH}_2 \\ \text{CH}_2 \end{array} \text{Pd} \begin{array}{c} \text{Cl} \\ \text{Cl} \end{array} \text{Pd} \begin{array}{c} \text{H}_2\text{C} \\ \text{H}_2\text{C} \end{array} \text{C} \begin{array}{c} \text{CH}_2 \\ \text{CH}_2\text{Cl} \end{array}$	25° in PhCN	257b
MeCH=C=CH ₂	PdCl ₂ (PhCN) ₂	$\text{ClC} \begin{array}{c} \text{CH}_2 \\ \text{CHMe} \end{array} \text{Pd} \begin{array}{c} \text{Cl} \\ \text{Cl} \end{array} \text{Pd} \begin{array}{c} \text{MeHC} \\ \text{H}_2\text{C} \end{array} \text{CCl}$	25° in C ₆ H ₆	177b
MeCH=C=CHMe	PdCl ₂ (PhCN) ₂	$\text{ClC} \begin{array}{c} \text{CHMe} \\ \text{CHMe} \end{array} \text{Pd} \begin{array}{c} \text{Cl} \\ \text{Cl} \end{array} \text{Pd} \begin{array}{c} \text{MeHC} \\ \text{MeHC} \end{array} \text{CCl}$	25° in C ₆ H ₆	177b
CH ₂ =CH—CH=CH ₂	PdCl ₂ (PhCN) ₂	$\text{HC} \begin{array}{c} \text{CH}_2 \\ \text{CH} \\ \\ \text{CH}_2\text{Cl} \end{array} \text{Pd} \begin{array}{c} \text{Cl} \\ \text{Cl} \end{array} \text{Pd} \begin{array}{c} \text{CH}_2\text{Cl} \\ \text{HC} \\ \\ \text{H}_2\text{C} \end{array} \text{CH}$	25°	245a, 259a
CH ₂ =CH—CH=CH ₂ (similarly with other conjugated dienes)	PdCl ₂ (PhCN) ₂ /MeOH	$\text{HC} \begin{array}{c} \text{CH}_2 \\ \text{CH} \\ \\ \text{CH}_2\text{OMe} \end{array} \text{Pd} \begin{array}{c} \text{Cl} \\ \text{Cl} \end{array} \text{Pd} \begin{array}{c} \text{CH}_2\text{OMe} \\ \text{HC} \\ \\ \text{H}_2\text{C} \end{array} \text{CH}$	25°	259a



^a Temperatures in Centigrade degrees.

^b Ar =

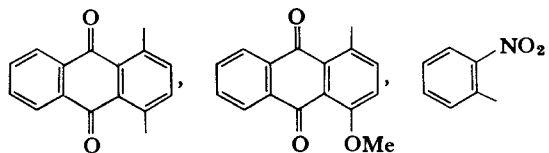



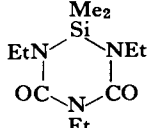


TABLE II
ISOCYANATE, ISOTHIOCYANATE, CARBODIIMIDE, KETENE, AND DIKETENE INSERTION REACTIONS

Reactants	Products	Experimental conditions ^a	References
<i>Reactions with MeNCO</i>			
Me ₃ SiNEt ₂	Me ₃ SiN(Me)CONEt ₂	80°–100°	220
Me ₃ SiNHPh	Me ₃ SiN(Me)CONHPh	35°	163
(Me ₃ Si) ₂ NMe	Me ₃ SiN(Me)CONMeSiMe ₃	—	163
Me ₃ SiN(Me)CON(Me)SiMe ₃	Me ₃ SiN(Me)CON(Me)CON(Me)SiMe ₃	35°	163
Bu ₃ SnOMe	Bu ₃ SnN(Me)COOMe	20°	25
(Bu ₃ Sn) ₂ O	Bu ₃ SnN(Me)COOSnBu ₃	20°	28
BuZnPPH ₂	BuZnN(Me)COPPh ₂	25°	213
<i>Reactions with EtNCO</i>			
PhBCl ₂	ClB[N(Et)COCl][N(Et)COPh]	10°	169
PhB(NMe ₂) ₂	PhB[N(Et)CONMe ₂] ₂	~ 20°	17
AlEt ₃	Et ₂ AlN(Et)COEt	> 40°	237
Me ₃ SiNEt ₂	Me ₃ SiN(Et)CONEt ₂	110°	87
Me ₃ SiN(CH ₂) ₂	Me ₃ SiN(Et)CON 	0°	248
(CH ₂) ₂ NSiMe ₂ N(CH ₂) ₂	 NCO(Et)NSiMe ₂ N(Et)CON 	40°	248
Me ₃ SiN(Et)CONEt ₂	Me ₃ SiN(Et)CON(Et)CONEt ₂	130°	87
(Me ₂ SiNH) ₃		60°–120°	86

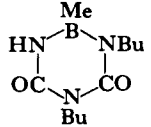
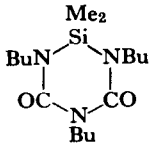
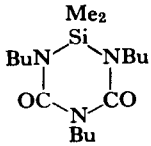
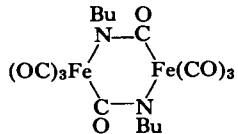
$(\text{Bu}_3\text{Sn})_2\text{O}$	$\text{Bu}_3\text{SnN}(\text{Et})\text{COOSnBu}_3$	20°	27, 28
Bu_3SnOMe	$\text{Bu}_3\text{SnN}(\text{Et})\text{COOMe}$	20°	25
<i>Reactions with BuNCO</i>			
$(\text{MeBNH})_3$		—	30
AlEt_3	$\text{Et}_2\text{AlN}(\text{Bu})\text{COEt}^b$	—	239
$\text{Me}_3\text{SiNEt}_2$	$\text{Me}_3\text{SiN}(\text{Bu})\text{CONEt}_2$	40°	87
$\text{Me}_3\text{SiN}(\text{CH}_2)_2$		0°	248
$(\text{Me}_2\text{SiNH})_3$		—	248
$\text{Me}_3\text{SiN}(\text{Bu})\text{CONEt}_2$	$\text{Me}_3\text{SiN}(\text{Bu})\text{CON}(\text{Bu})\text{CONEt}_2$	170°	87
Et_3SnOEt	$\text{Et}_3\text{SnN}(\text{Bu})\text{COOEt}$	25°	23, 25, 79
Bu_3SnOPh	$\text{Bu}_3\text{SnN}(\text{Bu})\text{COOPh}$	20°	25
$\text{As}(\text{NMe}_2)_3$	$\text{Me}_2\text{NAs}[\text{N}(\text{Bu})\text{CONMe}_2]_2$	—	269
$\text{Fe}_3(\text{CO})_{12}$		85°	181
$\text{Hg}(\text{OMe})_2$	$\text{Hg}[\text{N}(\text{Bu})\text{COOMe}]_2$	20°	79a

TABLE II—continued

280

M. F. LAPPERT and B. PROKAI

Reactants	Products	Experimental conditions ^a	References
<i>Reactions with iso-BuNCO</i>			
AlEt ₃	Et ₂ AlN(iso-Bu)COEt ^b	—	239
<i>Reactions with sec-BuNCO</i>			
AlEt ₃	Et ₂ AlN(sec-Bu)COEt ^b	—	239
<i>Reactions with tert-BuNCO</i>			
AlEt ₃	Et ₂ AlOC(Et):N-tert-Bu ^b	—	239
<i>Reactions with C₆H₁₁NCO</i>			
AlEt ₃	Et ₂ AlNC(C ₆ H ₁₁)COEt	—	237
<i>Reactions with C₆Cl₅NCO</i>			
AlEt ₃	Et ₂ AlNC(C ₆ Cl ₅)COEt	—	237
<i>Reactions with PhNCO</i>			
BCl ₃	ClB[N(Ph)COCl] ₂	5°	167
PhBCl ₂	ClB[N(Ph)COCl][N(Ph)COPh]	10°	167
Ph ₂ BCl	ClB[N(Ph)COPh] ₂	20°	167
PhB(NCS) ₂	SCNB[N(Ph)CONCS][N(Ph)COPh]	20°	148
Ph ₂ BNCS	PhB[N(Ph)CONCS][N(Ph)COPh]	20°	148
Ph ₃ B	PhB[N(Ph)COPh] ₂	20°	167
<i>p</i> -Tol ₃ B	<i>p</i> -TolB[N(Ph)COTol- <i>p</i>] ₂	25°	167
B(NMe ₂) ₃	B[N(Ph)CONMe ₂] ₃	20°	137
B ₂ (NMe ₂) ₄	B ₂ [N(Ph)CONMe ₂] ₄	~ 20°	137

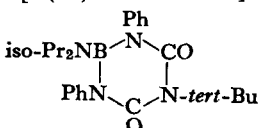
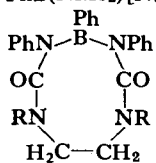
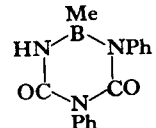
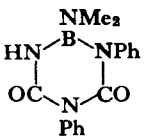
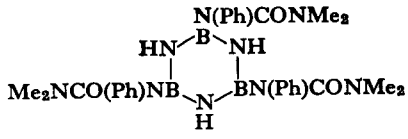
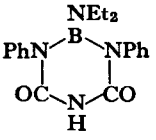
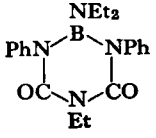
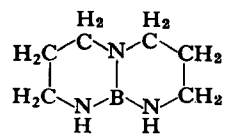
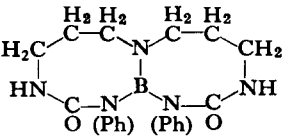
$\text{B}(\text{NH-}i\text{-tert-Bu})_3$	$\text{B}[\text{N}(\text{Ph})\text{CONH-}i\text{-tert-Bu}]_3$	$40^\circ\text{--}60^\circ$	68
$i\text{-tert-BuNHB}(\text{N-iso-Pr}_2)_2$		$40^\circ\text{--}60^\circ$	68
$i\text{-tert-BuN}[\text{BNH-}i\text{-tert-Bu}]_2$	$i\text{-tert-BuN}\{\text{B}[\text{N}(\text{Ph})\text{CONH-}i\text{-tert-Bu}]_2\}_2$	$40^\circ\text{--}60^\circ$	70
$\text{PhB}(\text{NHEt})_2$	$\text{PhB}[\text{N}(\text{Ph})\text{CONHEt}]_2$	$40^\circ\text{--}60^\circ$	71
$\text{PhB}(\text{NH-}i\text{-tert-Bu})_2$	$\text{PhB}[\text{N}(\text{Ph})\text{CONH-}i\text{-tert-Bu}]_2$	$40^\circ\text{--}60^\circ$	71
$\text{PhBCl}(\text{NMe}_2)$	$\text{PhB}(\text{Cl})[\text{N}(\text{Ph})\text{CONMe}_2]$	—	70
$\text{PhB}(\text{NHNHPh})_2$	$\text{PhB}[\text{N}(\text{Ph})\text{CONHNHPh}]_2$	$\sim 50^\circ$	70
$\text{PhB}(\text{NMe}_2)\text{NH-}i\text{-tert-Bu}$	$\text{PhB}(\text{NH-}i\text{-tert-Bu})[\text{N}(\text{Ph})\text{CONMe}_2]$	$\sim 50^\circ$	70
$\text{PhB}(\text{NMe}_2)_2$	$\text{PhB}[\text{N}(\text{Ph})\text{CONMe}_2]_2$	20°	17, 137
	$\text{PhB}(\text{NMe}_2)[\text{N}(\text{Ph})\text{CONMe}_2]$		
$\text{PhB}(\text{NRCH}_2)_2$ R = H, Bu		$\sim 120^\circ$	71
$\text{Ph}_2\text{B}(\text{NH-}i\text{-tert-Bu})$	$\text{Ph}_2\text{B}[\text{N}(\text{Ph})\text{CONH-}i\text{-tert-Bu}]$	$40^\circ\text{--}60^\circ$	71
$(\text{CH}_2\text{O})_2\text{BNEt}_2$	$(\text{CH}_2\text{O})_2\text{BN}(\text{Ph})\text{CONEt}_2$	—	70
$o\text{-C}_6\text{H}_4\text{O}_2\text{BNH-}i\text{-tert-Bu}$	$\text{C}_6\text{H}_4\text{O}_2\text{NB}(\text{Ph})\text{CONH-}i\text{-tert-Bu}$	25°	71
$o\text{-C}_6\text{H}_4\text{O}_2\text{BNEt}_2$	$\text{C}_6\text{H}_4\text{O}_2\text{BN}(\text{Ph})\text{CONEt}_2$	25°	170
$o\text{-C}_6\text{H}_4\text{O}_2\text{BOBu}$	$\text{C}_6\text{H}_4\text{O}_2\text{BN}(\text{Ph})\text{COOBu}$	25° ; 30 days	71
$o\text{-C}_6\text{H}_4\text{O}_2\text{BSEt}$	$\text{C}_6\text{H}_4\text{O}_2\text{BN}(\text{Ph})\text{COSEt}$	—	170
$o\text{-C}_6\text{H}_4\text{O}_2\text{BNCS}$	$\text{C}_6\text{H}_4\text{O}_2\text{BN}(\text{Ph})\text{CONCS}$	20°	148
$(\text{MeBNH})_3$		80°	18, 30

TABLE II—continued

Reactants	Products	Experimental conditions ^a	References
<i>Reactions with PhNCO—(continued)</i>			
(Me ₂ NBNH) ₃	 	60°	68
(Et ₂ NBNH) ₃		~60°	17
(Et ₂ NBNEt) ₃		60°–80°	68
		25°	92
AlEt ₃	Et ₂ AlN(Ph)COEt	—	142, 237, 239
AlEt ₂ Cl	ClAl[N(Ph)COEt]Et or ClAl[N(Ph)COEt] ₂	20°	142
AlBr ₃	Br ₂ AlN(Ph)COBr	20°	142

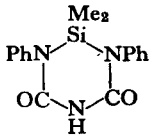
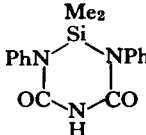
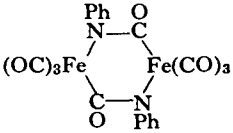
Me_3SiNHMe	$\text{Me}_3\text{SiN(Ph)CONHMe}$	$\sim 25^\circ$	163
$\text{Me}_3\text{SiNMe}_2$	$\text{Me}_3\text{SiN(Ph)CONMe}_2$	25°	163
$\text{Me}_3\text{SiNEt}_2$	$\text{Me}_3\text{SiN(Ph)CONEt}_2$	$\sim 40^\circ$	87, 220
$\text{Me}_3\text{SiNC}_5\text{H}_{10}$	$\text{Me}_3\text{SiN(Ph)CONC}_5\text{H}_{10}$	25°	87
$\text{Me}_3\text{SiN(CH}_2)_2$	$\text{Me}_3\text{SiN(Ph)CON(CH}_2)_2$	60°	248
$\text{Me}_2\text{PhSiNHPh}$	$\text{Me}_2\text{PhSiN(Ph)CONHPh}$	150°	163, 220
$\text{Me}_2\text{Si(NHEt)}_2$	$\text{Me}_2\text{Si[N(Ph)CONHEt]}_2$	60°	69
$\text{Me}_2\text{Si(NEt}_2)_2$	$\text{Me}_2\text{Si[N(Ph)CONEt}_2]_2$	$\sim 100^\circ$	69, 220
$\text{Me}_2\text{Si(NRCH}_2)_2$	$\text{Me}_2\text{Si[N(Ph)CONRCH}_2]_2$	-78°	69
R = H, Et, Bu			
$(\text{Me}_3\text{Si})_2\text{NH}$	$\text{Me}_3\text{SiN(Ph)CONHSiMe}_3$	$0^\circ-30^\circ$	87, 163, 292
$(\text{Me}_3\text{Si})_2\text{NMe}$	$\text{Me}_3\text{SiN(Ph)CON(Me)SiMe}_3$	$\sim 40^\circ$	163, 292
$(\text{Me}_3\text{Si})_2\text{NEt}$	$\text{Me}_3\text{SiN(Ph)CONEt}_2, \text{Me}_3\text{SiN(Ph)CON(Et)SiMe}_3$	$\sim 30^\circ$	292
$(\text{Me}_3\text{Si})_2\text{NPh}$	$\text{Me}_3\text{SiN(Ph)CON(Ph)SiMe}_3$	145°	163
$(\text{Me}_2\text{SiNH})_3$		$60^\circ-90^\circ$	248
$\text{Me}_3\text{SiN(Ph)CON(Me)SiMe}_3$	$\text{Me}_3\text{SiN(Ph)CON(Me)CON(Ph)SiMe}_3$	35°	163
$\text{Me}_3\text{SiN(Ph)CONEt}_2$	$\text{Me}_3\text{SiN(Ph)CON(Ph)CONEt}_2$	40°	87
$(\text{Me}_2\text{SiNH})_4$	 , $(\text{Me}_2\text{SiNH})_3$	$60^\circ-90^\circ$	248
$\text{Et}_3\text{GeNEt}_2$	$\text{Et}_3\text{GeN(Ph)CONEt}_2$	$\sim 25^\circ$	246
$\text{Me}_3\text{SnNMe}_2$	$\text{Me}_3\text{SnN(Ph)CONMe}_2$	25°	95, 154
Bu_3SnOMe	$\text{Bu}_3\text{SnN(Ph)COOMe}$	20°	23, 25, 26
$(\text{Et}_3\text{Sn})_2\text{O}$	$\text{Et}_3\text{SnN(Ph)COOSnEt}_3$	20°	28
$(\text{Pr}_3\text{Sn})_2\text{O}$	$\text{Pr}_3\text{SnN(Ph)COOSnPr}_3$	20°	24, 28

TABLE II—continued

284

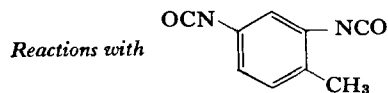
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Reactants	Products	Experimental conditions ^a	References
<i>Reactions with PhNCO—(continued)</i>			
(Bu ₃ Sn) ₂ O	Bu ₃ SnN(Ph)COOSnBu ₃ or [Bu ₃ SnN(Ph)] ₂ CO	25°	28, 86
Bu ₃ SnN(Ph)CON(Et)SnBu ₃	Bu ₃ SnN(Ph)CON(Et)CON(Ph)SnBu ₃	20°	29a
Ph ₃ SnPPh ₂	Ph ₃ SnN(Ph)COPPh ₂	—	258
As(NMe ₂) ₃	As[N(Ph)CONMe ₂] ₃	30°–40°	218
Bu ₃ Sb	Bu ₂ SbN(Ph)COBu	20°	54
EtZnNEt ₂	EtZnN(Ph)CONEt ₂	25°	212
EtZnNPh ₂	EtZnN(Ph)CONPh ₂	25°	212
Ti(OEt) ₄	(EtO) ₃ TiN(Ph)COOEt	0°	46
Ti(O-iso-Pr) ₄	(iso-PrO) ₃ TiN(Ph)COO-iso-Pr	0°	46
Ti(NMe ₂) ₄	Ti[N(Ph)CONMe ₂] ₄	20°	60
Ti(NMe ₂) ₄	(Me ₂ N) ₂ Ti[N(Ph)CONMe ₂] ₂	20°	60
[(PhCH ₂ O) ₂ CrNH ₂] _n	$ \begin{array}{c} \text{OCH}_2\text{Ph} \\ \\ \text{PhN} - \text{Cr} - \text{NH} \\ \quad \quad \\ \text{OC} - \text{N} - \text{CO} \\ \\ \text{Ph} \end{array} $	—	257
[ROCr(NH ₂) ₂] _n	$ \begin{array}{c} \text{RO} \\ \\ \text{HN} - \text{Cr} - \text{NCONHPh} \\ \quad \quad \\ \text{OC} - \text{N} - \text{CO} \\ \\ \text{Ph} \end{array} $	—	256

$\text{Fe}_3(\text{CO})_{12}$		85°	181
EtZnPPh_2	EtZn(Ph)COPPh_2	25°	213
PhZnPPh_2	PhZn(Ph)COPPh_2	25°	213
Hg(OMe)_2	Hg[N(Ph)COOMe]_2	20°	79a
PhHgOMe	PhHgN(Ph)COOMe	20°	79a

Reactions with 1-C₁₀H₇NCO

BCl_3	$\text{ClB[N(1-C}_{10}\text{H}_7\text{)COCl]}_2$	5°	167
Et_3SnOEt	$\text{Et}_3\text{SnN(1-C}_{10}\text{H}_7\text{)COOEt}$	20°	23, 25
$(\text{Bu}_3\text{Sn})_2\text{O}$	$\text{Bu}_3\text{SnN(1-C}_{10}\text{H}_7\text{)COOSnBu}_3$ or $[\text{Bu}_3\text{SnN(1-C}_{10}\text{H}_7\text{)}]_2\text{CO}$	20°	28
Bu_3SnOMe	$\text{Bu}_3\text{SnN(1-C}_{10}\text{H}_7\text{)COOMe}$	20°	23, 25
$\text{Bu}_3\text{SnN(Me)CON(Ph)SnBu}_3$	$\text{Bu}_3\text{SnN(1-C}_{10}\text{H}_7\text{)CON(Ph)SnBu}_3$	20°	29a
Bu_3PbOMe	$\text{Bu}_3\text{PbN(1-C}_{10}\text{H}_7\text{)CO}_2\text{Me}$	20°	79b
Ph_3PbOMe	$\text{Ph}_3\text{PbN(1-C}_{10}\text{H}_7\text{)CO}_2\text{Me}$	20°	79b
Ti(OEt)_4	$(\text{EtO})_3\text{TiN(1-C}_{10}\text{H}_7\text{)COOEt}$	0°	46



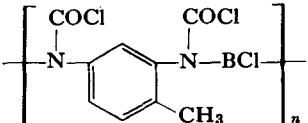
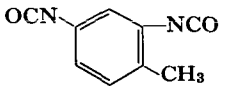
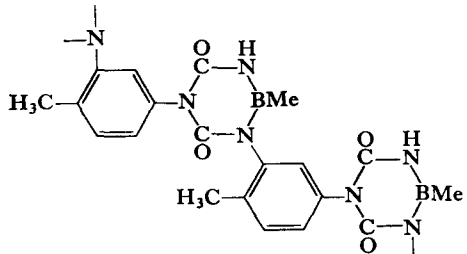
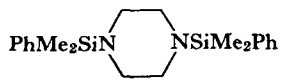
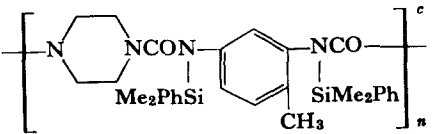
BCl_3		5°	167
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TABLE II—continued

286

Reactants	Products	Experimental conditions ^a	References
<p>Reactions with</p>  <p>—(continued)</p>			
<p>(MeBNH)₃</p>		—	30
		100°	162
<p>Reactions with CH₂=CHNCO</p> <p>(Me₃Si)₂NH</p>	<p>CH₂=CHN(SiMe₃)CONHCH=CH₂</p>	—	221
<p>Reactions with <i>o</i>-C₆H₄O₂BNCO</p> <p><i>o</i>-C₆H₄O₂BNH-<i>tert</i>-Bu</p>	<p><i>o</i>-C₆H₄O₂BNBO₂C₆H₄-<i>o</i></p> <p style="text-align: center;"> </p> <p style="text-align: center;">CONH-<i>tert</i>-Bu</p>	40°–60°	71

M. F. LAPPERT and B. PROKAI

*Reactions with MeNCS*

AlEt ₃	Et ₂ AlN(Me)CSEt	—	237
Me ₃ SiNEt ₂	Me ₃ SiN(Me)CSNEt ₂	80°–100°	220
Me ₂ Si(NEt ₂) ₂	Me ₂ (Et ₂ N)SiN(Me)CSNEt ₂	~ 100°	220
As(NMe ₂) ₃	As[(Me)CSNMe ₂] ₃	30°–50°	218
EtZnNPh ₂	EtZnN(Me)CSNPh ₂	—	212

Reactions with RNCS (R = n-Bu, iso-Bu, tert-Bu, or CH=CHCH₂)

AlEt ₃	Et ₂ AlN(R)CSEt (not isolated, but hydrolyzed)	—	237, 239
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Reactions with PhNCS

PhBCl ₂	ClB[N(Ph)CSCl][N(Ph)CSPH]	20°	167
PhB(NMe ₂) ₂	PhB[N(Ph)CSNMe ₂] ₂ , Ph(NMe ₂)B[N(Ph)CSNMe ₂]	20°	17
B(NMe ₂) ₃	B[N(Ph)CSNMe ₂] ₃	20°	137
B ₂ (NMe ₂) ₄	B ₂ [N(Ph)CSNMe ₂] ₄	20°	137
<i>o</i> -C ₆ H ₄ O ₂ BNH- <i>tert</i> -Bu	<i>o</i> -C ₆ H ₄ O ₂ BN(Ph)CSNH- <i>tert</i> -Bu	20°	170
AlBr ₃	Br ₂ AlN(Ph)CSBr	20°	142
AlEt ₃	Et ₂ AlN(Ph)CSEt	20°	142, 239
Me ₃ SiNHMe	Me ₃ SiN(Ph)CSNHMe	25°	163
Me ₃ SiNMe ₂	Me ₃ SiN(Ph)CSNMe ₂	25°	163
Me ₃ SiNEt ₂	Me ₃ SiN(Ph)CSNEt ₂	40°–50°	218
Me ₂ PhSiN- <i>tert</i> -BuH	Me ₂ PhSiN(Ph)CSN- <i>tert</i> -BuH	25°	163
Me ₂ Si(NREt) ₂	Me ₂ Si[N(Ph)CSNHEt] ₂	80°	69
R = H or Et			
(Me ₃ Si) ₂ NMe	Me ₃ SiN(Ph)CSN(Me)SiMe ₃	35°	163
Et ₃ GeNMe ₂	Et ₃ GeN(Ph)CSNMe ₂	25°	246
Me ₃ SnNMe ₂	Me ₃ SnN(Ph)CSNMe ₂	20°	95, 155

TABLE II—continued

Reactants	Products	Experimental conditions ^a	References
<i>Reactions with PhNCO—(continued)</i>			
Bu ₃ SnOMe	Bu ₃ SnN(Ph)CSOMe	20°	23
Et ₃ SnOEt	Et ₃ SnSC(NPh)OEt	20°	214
Ph ₃ PbOMe	Ph ₃ PbSC(NPh)OMe	20°	79b
Ph ₃ SnPPh ₂	Ph ₃ SnN(Ph)CSPPH ₂	—	258
EtZnNEt ₂	EtZnN(Ph)CSNEt ₂	25°	212
EtZnNPh ₂	EtZnN(Ph)CSNPh ₂	25°	212
PhZnNPh ₂	PhZnN(Ph)CSNPh ₂	25°	212
Ti(NMe ₂) ₄	Ti[N(Ph)CSNMe ₂] ₄	20°	60
Ti(NEt ₂) ₄	(Et ₂ N) ₂ Ti[N(Ph)CSNEt ₂] ₂	20°	61
EtZnPPH ₂	EtZnN(Ph)CSPPH ₂	25°	213
PhZnPPH ₂	PhZnN(Ph)CSPPH ₂	25°	213
Hg(OMe) ₂	HgN(Ph)CSOMe	20°	79a
<i>Reactions with p-CH₃C₆H₄N=C=NC₆H₄CH₃-p</i>			
BCl ₃	ClB[N(Ar)C(=NAr)Cl] ₂ ^d	-5°	149
BBr ₃	BrB[N(Ar)C(=NAr)Br] ₂ ^d	-5°	149
MeOBCl ₂	MeO(Cl)BN(Ar)C(=NAr)Cl ^d	20°	149
PhBCl ₂	ClB $\begin{matrix} \diagup \text{N(Ar)C(=NAr)Cl} \\ \diagdown \text{N(Ar)C(=NAr)Ph} \end{matrix}$ ^d	10°	149
PhB(OMe) ₂	Ph(MeO)BN(Ar)C(=NAr)OMe ^d	25°	149
PhB(NEt ₂)S- <i>n</i> -Bu	Ph(<i>n</i> -BuS)BN(Ar)C(=NAr)NEt ₂ ^d	20°	149
(MeO) ₂ BCl	(MeO) ₂ BN(Ar)C(=NAr)Cl ^d	20°	149
(Et ₂ N) ₂ BCl	Cl(Et ₂ N)BN(Ar)C(=NAr)NEt ₂ ^d	20°	149
Ph ₂ BCl	ClB[N(Ar)C(=NAr)Ph] ₂ ^d	25°	149
Ph ₂ BOMe	Ph ₂ BN(Ar)C(=NAr)OMe ^d	20°	149
Ph ₂ BNEt ₂	Ph ₂ BN(Ar)C(=NAr)NEt ₂ ^d	20°	149
Ph ₂ BS- <i>n</i> -Bu	Ph ₂ BN(Ar)C(=NAr)S- <i>n</i> -Bu ^d	20°	149

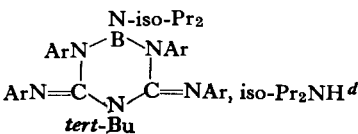
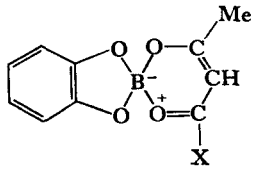
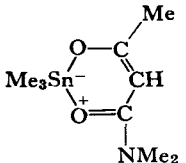
(iso-Pr ₂ N) ₂ BNH- <i>tert</i> -Bu		220°	149
<i>o</i> -C ₆ H ₄ O ₂ BNEt ₂	<i>o</i> -C ₆ H ₄ O ₂ BN(Ar)C(=NAr)NEt ₂ ;	20°	149
<i>o</i> -C ₆ H ₄ O ₂ BS- <i>n</i> -Bu	<i>o</i> -C ₆ H ₄ O ₂ BN(Ar)C(=NAr)N(Ar)C(=NAr)NEt ₂ ^d	20°	149
<i>o</i> -C ₆ H ₄ O ₂ BS- <i>n</i> -Bu	<i>o</i> -C ₆ H ₄ O ₂ BN(Ar)C(=NAr)S- <i>n</i> -Bu ^d	20°	149
Me ₃ SnNMe ₂	Me ₃ SnN(Ar)C(=NAr)NMe ₂ ^e	25°	95, 155
Bu ₃ SnOMe	Bu ₃ SnN(Ar)C(=NAr)OMe ^e	25°	24
(Bu ₃ Sn) ₂ O	Bu ₃ SnN(Ar)C(=NAr)OSnBu ₃ ^{e, f}	25°	27
Ph ₃ PbOMe	Pb ₃ PbN(Ar)C(=NAr)OMe ^e	25°	79b
Ti(NMe ₂) ₄	(Me ₂ N) ₂ Ti[NArC(=NAr)NMe ₂] ₂ ^g	20°	61
<i>Reactions with CH₂=C=O</i>			
PhBCl ₂	Cl ₂ BCH ₂ COPh, or PhClBCH ₂ COCl	10°	169
Ph ₂ BCl	Ph ₂ BCH ₂ COCl or PhClBCH ₂ COPh	10°	169
<i>o</i> -C ₆ H ₄ O ₂ BX	<i>o</i> -C ₆ H ₄ O ₂ BCH ₂ COX	20°	142, 170
X = Cl, NMe ₂ , NEt ₂ , N-iso-Pr ₂			
Me ₃ SiNHBu	Me ₃ SiCH ₂ CONHBu	20°	176
(Me ₃ Si) ₂ NH	(Me ₃ Si) ₂ NCOCH ₃	—	176
Me ₃ SnMe ₂	Me ₃ SnCH ₂ CONMe ₂	20°	95
Et ₃ SnOR	Et ₃ SnCH ₂ COOR	20°	178
R = Me, Et, Pr			
Pr ₃ SnOR	Pr ₃ SnCH ₂ COOR	20°	178
R = Me, Et, Pr			
Bu ₃ SnOEt	Bu ₃ SnCH ₂ COOEt	20°	24
Et ₂ Sn(OR) ₂	Et ₂ Sn(CH ₂ COOR) ₂	~ 5°	232
R = Me, Et			
Pr ₂ Sn(OR) ₂	Pr ₂ Sn(CH ₂ COOR) ₂	~ 5°	232
R = Me, Et			
Sb(OR) ₃	Sb(CH ₂ COOR) ₃	25°	89
R = Et, Pr, Bu			
Hg(OMe) ₂	Hg(CH ₂ COOMe) ₂	20°	177c

TABLE II—continued

290

M. F. LAPPERT and B. PROKAI

Reactants	Products	Experimental conditions ^a	References
Reactions with $\text{CH}_2=\text{C} \begin{array}{c} \text{---} \text{O} \\ \quad \\ \text{CH}_2 \text{---} \text{C}=\text{O} \end{array}$			
$o\text{-C}_6\text{H}_4\text{O}_2\text{BX}$ $\text{X} = \text{NEt}_2, \text{Cl}, \text{OMe}$		25°	142
$\text{B}(\text{NRR}')_3$ $\text{RR}' = \text{Me}_2 \text{ or } \text{HBu-tert}$	$\text{B}(\text{NRR}')_3 \cdot 3(\text{CH}_2\text{CO})^h$	25°	142
$\text{AlCl}_3 \cdot \text{OEt}_2$	$\text{Cl}_2\text{AlOC}(\text{Me})\text{CHCOCl} \cdot (\text{OEt}_2)^h$	25°	142
$\text{Me}_3\text{SnNMe}_2$		25°	142

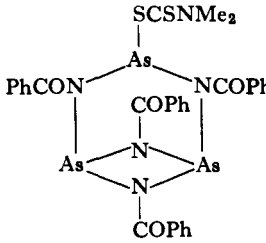
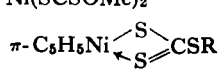
^a Temperatures in Centigrade degrees.^b Not isolated, but hydrolyzed.^c Polymers of this nature were obtained by using other similar reagents and substrates.^d $\text{Ar} = p\text{-CH}_3\text{C}_6\text{H}_4\text{-}$.^e $\text{Ar} = \text{C}_{10}\text{H}_7\text{-}$.^f $\text{Ar} = \text{Ph}$.^g Also for $\text{Ti}(\text{NMe}_2)_4/\text{C}_6\text{H}_{11}\text{N}=\text{C}=\text{NC}_6\text{H}_{11}$.^h Structure not yet elucidated.

TABLE III

CARBON DIOXIDE, CARBONYL SULFIDE, CARBON DISULFIDE, AND *N*-THIONYLAMIDE
INSERTION REACTIONS

Reactants	Products	Experimental conditions ^a	References
<i>Reactions of CO₂</i>			
(<i>tert</i> -BuNH) ₃ B		20°; <i>tert</i> -BuNH ₂	68
PhB(NHEt) ₂	PhB(OCONHEt) ₂	25°	170
PhB(NH- <i>tert</i> -Bu) ₂	PhB(OCONH- <i>tert</i> -Bu) ₂	25°	70
<i>o</i> -C ₆ H ₄ O ₂ BNEt ₂	<i>o</i> -C ₆ H ₄ O ₂ BOCONEt ₂	25°; Et ₂ NH	170
<i>o</i> -C ₆ H ₄ O ₂ BNH- <i>tert</i> -Bu	<i>o</i> -C ₆ H ₄ O ₂ BOCONH- <i>tert</i> -Bu	25°; Et ₂ NH	170
<i>tert</i> -Bu ₃ Al · Et ₂ O	<i>tert</i> -Bu ₂ AlOCO- <i>tert</i> -Bu	100°	171
Me ₃ SiNEt ₂	Me ₃ SiOCONEt ₂	20°; Et ₂ NH	37, 218
Me ₂ Si(NHEt) ₂	Me ₂ Si(OCONHEt) ₂	20°	69
Me ₂ Si(NEt ₂) ₂	Me ₂ Si(OCONEt ₂) ₂	30°; Et ₂ NH	37, 69, 216
Et ₃ GeNEt ₂	Et ₃ GeOCONEt ₂	25°	246
Me ₃ SnNMe ₂	Me ₃ SnOCONMe ₂	20°	95, 154
Bu ₃ SnOMe	Bu ₃ SnOCOOMe	20°	24
As(NMe ₂) ₃	As(OCONMe ₂) ₃ , (Me ₂ N) ₂ AsOCONMe ₂	20°–40°	218, 219 217
Ti(NMe ₂) ₄	Ti(OCONMe ₂) ₄	20°	60
(MeHg) ₂ O	MeHgOCOOHgMe	—	111a
<i>Reactions of COS</i>			
Ph ₃ SnPPh ₂	Ph ₃ SnSCOPPh ₂	—	258
<i>Reactions of CS₂</i>			
PhB(NEt ₂) ₂	PhB(NEt ₂)SCSNEt ₂	—	70
AlEt ₃	Et ₂ AlSCSEt, (Et ₂ Al) ₂ S, Et ₃ CSAlEt ₂	40°–50°	238a
Me ₃ SiNMe ₂	Me ₃ SiSCSNMe ₂	20°; Et ₂ NH	37
Me ₃ SiNEt ₂	Me ₃ SiSCSNEt ₂	20°; Et ₂ NH	36, 37
Me ₂ Si(NHEt) ₂	Me ₂ (NHEt)SiSCSNHEt	20°	69
Me ₂ Si(NEt ₂) ₂	Me ₂ (NEt ₂)SiSCSNEt ₂	20°; Et ₂ NH	69
Me ₃ SiAsMe ₂	Me ₃ SiSCSAsMe ₂	—	245b
Et ₃ GeNMe ₂	Et ₃ GeSCSNMe ₂	20°	246
Et ₃ GeNEt ₂	Et ₃ GeSCSNEt ₂	20°	246
Me ₃ SnNMe ₂	Me ₃ SnSCSNMe ₂	20°	95, 154
Bu ₃ SnOMe	Bu ₃ SnSCSOMe	25°	24
Ph ₃ SnPPh ₂	Ph ₃ SnSCSPPPh ₂	—	258
Ph ₃ SnPPh ₂	Ph ₃ SnSCCl ₂ PPh ₂ ^b	—	258
Ph ₃ SnPPh ₂	Ph ₃ SnSC(NH ₂) ₂ PPh ₂ ^c	—	258

TABLE III—continued

Reactants	Products	Experimental conditions ^a	References
<i>Reactions of CS₂—(continued)</i>			
Ph ₃ PbOMe	Ph ₃ PbSCSOMe	20°	79b
As(NMe ₂) ₃	As[SCSNMe ₂] ₃	20°–40°	217, 270, 271
As(NBu ₂) ₃	As[SCSNBu ₂] ₃	~40°	217, 270, 271
As[N(C ₅ H ₁₀) ₂] ₃	As[SCSN(C ₅ H ₁₀) ₂] ₃	—	271
MeAs(NMe ₂) ₂	MeAs(SCSNMe ₂) ₂	20°–40°	217
Sb(NMe ₂) ₃	Sb(SCSNMe ₂) ₃	20°–40°	217
[Me ₂ NAsNCOPh] _n		80°	269
Ti(NMe ₂) ₄	As(SCSNMe ₂) ₃ Ti(SCSNMe ₂) ₄	—	35
Ti(NEt ₂) ₄	Ti(SCSNMe ₂) ₄	—	35
Ti(NPr ₂) ₄	Ti(SCSNPr ₂) ₄	—	35
Zr(NMe ₂) ₄	Zr(SCSNMe ₂) ₄	—	35
Zr(NEt ₂) ₄	Zr(SCSNMe ₂) ₄	—	35
Zr(NPr ₂) ₄	Zr(SCSNPr ₂) ₄	—	35
Nb(NMe ₂) ₅	Nb(SCSNMe ₂) ₄	—	35
Ta(NMe ₂) ₅	Ta(SCSNMe ₂) ₅	—	35
Ni(OMe) ₂	Ni(SCSOMe) ₂	20°	207
(π-C ₅ H ₅ NiSR) ₂ R = Me, Et		25°	22
CuSR R = Et, Bu	CuSCSSR	25°	81
RHgOH R = Me, <i>p</i> -CH ₃ C ₆ H ₄	RHgSCSOMe	MeOH; trace NaOH	164b
RHgOH R = Me, Et, <i>n</i> -Pr, <i>n</i> -Bu, PhCH ₂ , <i>p</i> -CH ₃ C ₆ H ₄	RHgSCSOEt	EtOH; trace NaOH	164b
(PhHg) ₂ S	(PhHgS) ₂ CS	—	230a
<i>Reactions of PhNSO</i>			
Me ₃ SnNMe ₂	Me ₃ SnN(Ph)SONMe ₂	20°	95

^a Temperatures in Centigrade degrees.^b CSCI₂ was the reagent.^c CS(NH₂)₂ was the reagent.

TABLE IV
SULFUR TRIOXIDE, SELENIUM TRIOXIDE, AND SULFUR DIOXIDE INSERTION REACTIONS

Reactants	Products	Experimental conditions ^a	References
<i>Reactions of SO₃</i>			
Me ₂ SiF ₂	Me ₂ Si(OSO ₂ F)F, Me ₂ Si(OSO ₂ F) ₂	−30° to 20°	249
Me ₂ SiFCl	Me ₂ Si(OSO ₂ F)(OSO ₂ Cl)	−30° to 20°	249
Me ₃ SiF	Me ₃ SiOSO ₂ F	−30° to 20°	249
MeSiCl ₃	MeSiCl ₂ (OSO ₂ Cl)	10°	253, 254
Me ₂ SiCl ₂	Me ₂ SiCl(OSO ₂ Cl), Me ₂ Si(OSO ₂ Cl) ₂	−15° to −5°	253, 254
Me ₃ SiCl	Me ₃ SiOSO ₂ Cl	−30°	253, 254
Me ₃ SiNEt ₂	Me ₃ SiOSO ₂ NEt ₂	25°	253
Me ₂ Si(OEt) ₂	Me ₂ Si(OEt)OSO ₂ OEt	0° to 70°	34
(Me ₂ SiO) ₃	Me ₂ Si(OSO ₂ O) ₂ SiMe ₂	—	252
Me ₃ SiOMe	Me ₃ SiOSO ₂ OMe	−78°	251
<i>m</i> -MeC ₆ H ₄ SiMe ₃	<i>m</i> -MeC ₆ H ₄ SO ₂ OSiMe ₃	0° to 70°	34
<i>p</i> -, <i>m</i> -, and <i>o</i> -Me ₃ SiC ₆ H ₄ SiMe ₃	<i>p</i> -, <i>m</i> -, and <i>o</i> -Me ₃ SiC ₆ H ₄ SO ₂ OSiMe ₃	0° to 70°	34, 82
<i>p</i> -, and <i>m</i> -Ph ₃ SiC ₆ H ₄ SiMe ₃	<i>p</i> -, and <i>m</i> -Ph ₃ SiC ₆ H ₄ SO ₂ OSiMe ₃	0° to 70°	34
<i>p</i> -F ₂ MeSiC ₆ H ₄ SiMe ₃	<i>p</i> -F ₂ MeSiC ₆ H ₄ SO ₂ OSiMe ₃	0° to 70°	34
<i>p</i> -Et ₃ GeC ₆ H ₄ GeEt ₃	<i>p</i> -Et ₃ GeC ₆ H ₄ SO ₂ OG ₂ Et ₃	0°	33
<i>Reactions of SeO₃</i>			
Me ₃ SiCl	Me ₃ SiOSeO ₂ Cl	−40°	255
Me ₃ SnCl	Me ₃ SnCl ⁺ SeO ₃ [−]	−78°	255
<i>Reactions of SO₂</i>			
R ₃ Al	R ₂ AlOSOR (not isolated)	—	67, 293
R = Et, C ₈ H ₁₇ , C ₁₂ H ₂₅			
Et ₃ Al·OEt ₂	Al(OSOEt) ₃	−75°	6
Me ₃ SnNMe ₂	Me ₃ SnOSONMe ₂	20°	95
Ti(NMe ₂) ₄	OTi(OSONMe ₂) ₂	20°	61
π-C ₅ H ₅ Mo(CO) ₃ Me	π-C ₅ H ₅ Mo(CO) ₃ SO ₂ Me	−60° to 40°	288a
(OC) ₅ MnR	(OC) ₅ MnSO ₂ R	−75°	117a
π-C ₅ H ₅ Fe(CO) ₂ Me	π-C ₅ H ₅ Fe(CO) ₂ SO ₂ Me	−60° to −40°	19
π-C ₅ H ₅ Fe(CO) ₂ Et	π-C ₅ H ₅ Fe(CO) ₂ SO ₂ Et	−60° to −40°	19
π-C ₅ H ₅ Fe(CO) ₂ Ph	π-C ₅ H ₅ Fe(CO) ₂ SO ₂ Ph	−60° to −40°	19
π-C ₅ H ₅ Fe(CO) ₂ CH ₂ Ph	π-C ₅ H ₅ Fe(CO) ₂ SO ₂ CH ₂ Ph	−60° to −40°	288a
CoCl ₂ /KCN	[(NC) ₅ CoOSOC(CN) ₅] ^{6−}	—	272
Ph ₂ Hg	PhHgSO ₂ Ph	−40°	288a
Et ₂ Hg	EtHgSO ₂ Et	—	288b
(PhCH ₂) ₂ Hg	PhCH ₂ HgSO ₂ CH ₂ Ph	—	288b

^a Temperatures in Centigrade degrees.

TABLE V
ALDEHYDE AND KETONE INSERTION REACTIONS

Reactants		Products	Experimental conditions ^a	References
MX _n	Carbonyl compound			
BCl ₃	XCCl ₂ CHO X = Cl or H	B(OCHClCCl ₂ X) ₃	-78°	90
BCl ₃	$\begin{array}{c} \text{CF}_2-\text{C}=\text{O} \\ \\ \text{CF}_2-\text{CF}_2 \end{array}$	B[OCCl(CF ₂) ₃] ₃	25°	197, 227
BuBCl ₂	$\begin{array}{c} \text{CF}_2-\text{C}=\text{O} \\ \\ \text{CF}_2-\text{CF}_2 \end{array}$	BuB[OCCl(CF ₂) ₃] ₂	25°	197
PhBCl ₂	CClF ₂ COCClF ₂	PhB(OCClCClF ₂) ₂	25°	197
PhBCl ₂	$\begin{array}{c} \text{CF}_2-\text{C}=\text{O} \\ \\ \text{CF}_2-\text{CF}_2 \end{array}$	PhB[OCCl(CF ₂) ₃] ₂	25°	197, 227
PhBCl ₂	$\begin{array}{c} \text{CF}_2-\text{C}=\text{O} \\ \\ \text{CF}_2-\text{C}=\text{O} \end{array}$	$\begin{array}{c} \text{Ph} \begin{array}{l} \diagup \text{O}-\text{CCl}-\text{CF}_2 \\ \diagdown \text{O}-\text{CCl}-\text{CF}_2 \end{array} \end{array}$	25°	197, 227
Et ₃ B	CBr ₃ CHO	Et ₂ BOCH=CBr ₂ , EtB(OCH=CBr ₂) ₂	90°-120°	186a
Bu ₃ B	PhCHO	Bu ₂ BOCH ₂ Ph, EtCH=CH ₂	100°-150°	189
iso-Bu ₃ B	PhCHO	iso-BuB(OCH ₂ Ph) ₂ , Me ₂ C=CH ₂	100°-150°	189
iso-Am ₃ B	PhCHO	iso-Am ₂ BOCH ₂ Ph, EtCHMeCH=CH ₂	100°-150°	189
(C ₆ H ₁₃) ₃ B	PhCHO	(C ₆ H ₁₃) ₂ BOCH ₂ Ph,	100°-150°	189

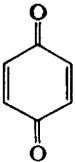
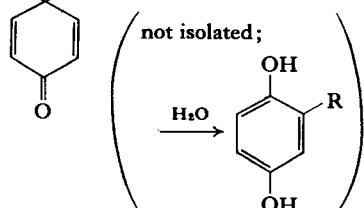

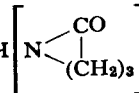
$\left(\text{Cyclohexyl-CH}_2\right)_3\text{B}$	PhCHO	$\left(\text{Cyclohexyl-CH}_2\right)_2\text{BOCH}_2\text{Ph,}$	125°–150°	189
$(\text{CH}_2=\text{CHCH}_2)_3\text{B}$	MeCHO	$\text{Cyclohexyl-CH=CH}_2$		
$(\text{CH}_2=\text{CHCH}_2)_3\text{B}$	EtCHO	$(\text{CH}_2=\text{CHCH}_2)_2\text{BOCH}_2\text{Me, C}_6\text{H}_8$	—	266
$(\text{CH}_2=\text{CHCH}_2)_3\text{B}$	PhCHO	$\text{B(OCHEtCH}_2\text{CH=CH}_2)_3,$	–70°–170°	187
$(\text{CH}_2=\text{CHCH}_2)_3\text{B}$	Me ₂ CO	$\text{C}_3\text{H}_5\text{B(OCHEtCH}_2\text{CH=CH}_2)_2,$		
R_3B		$(\text{C}_3\text{H}_5)_2\text{B(OCHEtCH}_2\text{CH=CH}_2)$	–70°–170°	187
		$\text{B(OCHPhCH}_2\text{CH=CH}_2)_3,$	60°–80°	187
		$\text{C}_3\text{H}_5\text{B(OCHPhCH}_2\text{CH=CH}_2)_2$		
		$\text{C}_3\text{H}_5\text{B(OCMe}_2\text{CH}_2\text{CH=CH}_2)_2$		
		$\text{R}_2\text{BO} \begin{array}{c} \diagup \text{R} \\ \diagdown \end{array}$		
			35°	118, 119
AlEt ₃	Me ₂ NCHO	Me ₂ NCH(Et)OAlEt ₂	0°	238a
Me ₃ SiNMeCOH	RCHO	(not isolated, but hydrolyzed)		
	R = Pr, Ph	Me ₃ SiOCH(NMeCOH)	25°	20

TABLE V—continued

Reactants		Products	Experimental conditions ^a	References
MX _n	Carbonyl compound			
Me ₃ SiNMeCOMe	RCHO R = Et, Ph, <i>p</i> -MeC ₆ H ₄	Me ₃ SiOCH(NMeCOMe)R	Heat	20
Me ₃ SiN 	PhCHO	Me ₃ SiOCH  Ph	Heat	20
Me ₃ SiCH ₂ CO ₂ Et	RCHO R = Ph, <i>p</i> -MeOC ₆ H ₄ , <i>p</i> -NO ₂ C ₆ H ₄	Me ₃ SiOCH(CH ₂ CO ₂ Et)R	160°–180°, NaOH or K[Al(OMe) ₄]	21
Me ₃ SiCH ₂ CN	RCHO R = Ph, <i>p</i> -NO ₂ C ₆ H ₄	Me ₃ SiOCH(CH ₂ CN)R	160°–180°, NaOH or K[Al(OMe) ₄]	21
Me ₃ SiCH ₂ CN	EtCR ₂ CHO R = H, Me	Me ₃ SiOCH(CH ₂ CN)CR ₂ Et	160°–180°, NaOH	21
Me ₃ SiOH	(CF ₃) ₂ CO	Me ₃ SiOC(CF ₃) ₂ OH	20°	147a
Ph ₂ Si(OH) ₂	(CF ₃) ₂ CO	Ph ₂ Si[OC(CF ₃) ₂ OH] ₂ → (Ph ₂ SiO) ₃ , (Ph ₂ SiO) ₄	20°	147a
Bu ₃ SnOMe	RCHO R = CCl ₃ , ⁿ Bu, Me, Pr, iso-	Bu ₃ SnOCH(OMe)R	25°	24, 80
Et ₃ SnCH ₂ COMe	PhCHO	Et ₃ SnOCH(CH ₂ COMe)Ph	25°	233
(Bu ₃ Sn) ₂ O	CCl ₃ CH ₂ O	Bu ₃ SnOCH(OSnBu ₃)CCl ₃	25°	24, 80
Bu ₃ SnOMe	CCl ₃ CHO	Bu ₃ Sn[OCH(CCl ₃)] _n OMe	—	79, 80
Bu ₃ SnOMe	(CCl ₃) ₂ CO	Bu ₃ SnOC(CCl ₃) ₂ OMe	25°	80a
Ph ₃ PbOMe	CCl ₃ CHO	Ph ₃ PbOCH(CCl ₃)OMe	25°	79b
(Ph ₃ Pb) ₂ O	CCl ₃ CHO	Ph ₃ PbOCH(CCl ₃)OPbPh ₃	25°	79b

^a Temperatures in Centigrade degrees.

TABLE VI
NITRIC OXIDE, DINITROGEN TETROXIDE, NITROSOBENZENE, AND NITROMETHANE
INSERTION REACTIONS

Reactants	Products	Experimental conditions ^a	References
<i>Reactions of NO</i>			
Et ₃ B	Et ₂ BN $\begin{smallmatrix} \diagup \text{NO} \\ \diagdown \text{OEt} \end{smallmatrix}$	-30°	41
	$\left\{ \begin{array}{l} \text{Et}_2\text{BON} \begin{smallmatrix} \diagup \text{Et} \\ \diagdown \text{BEt}_2 \end{smallmatrix}, \\ \text{Et}_2\text{BONEt}_2 \end{array} \right.$	+70°	41
Bu ₃ B	Bu ₂ BONBu ₂ , Bu ₂ BN $\begin{smallmatrix} \diagup \text{OBu} \\ \diagdown \text{NO} \end{smallmatrix}$, Bu ₂ BN(Bu)OBBu ₂ , + C ₄ H ₈ + C ₄ H ₁₀	—	147
R ₃ B R = iso-Bu, Ph	1:2 NO adducts	20°	1, 2
Et ₂ AlCl	1:2 NO adduct	20°	1, 2
Et ₃ Al · OEt ₂	Cu[ON(NO)Et] ₂ after addition of CuO	—	6
<i>Reaction of N₂O₄</i>			
Et ₃ Al	1:1 adduct	—	6
<i>Reactions of Nitrosobenzene</i>			
Bu ₃ B	1:1 adduct ^b	20°	147, 289
Me ₃ SnNMe ₂	Me ₃ SnN(Ph)ONMe ₂	20°	96
<i>Reactions of Nitromethane</i>			
B(NH- <i>tert</i> -Bu) ₃	1:3 adduct ^c	Et ₂ O; 20°	70
<i>o</i> -C ₆ H ₄ O ₂ BNMe ₂	1:1 adduct ^c	Et ₂ O; 20°	70
<i>o</i> -C ₆ H ₄ O ₂ BNH- <i>tert</i> -Bu	1:1 adduct ^c	Et ₂ O; 20°	170

^a Temperatures in Centigrade degrees.

^b See Section III, F.

^c These probably have structure $\begin{array}{c} \text{O} \\ \uparrow \\ \text{>B-O-N-N<} \\ | \\ \text{Me} \end{array}$; if the reactions are carried out in

absence of solvent, then amine is readily lost (70, 170).

TABLE VII
 NITRILE INSERTION REACTIONS^a

Reactants		Products	Experimental conditions ^b	References
MX _n	RCN			
BCl ₃	CF ₃ CN	[CF ₃ C(Cl)BCl ₂] ₂	20°	61b
R BSR'	MeCN	[R ₂ BN:C(Me)SR'] ₂	20°	188a
R = Pr and R' = Et; or R' = Bu and R = Pr, Bu, or Ph				
Me ₃ Al	MeCN	Me ₂ AlN: CMe ₂	120°–150°	150
Me ₃ Al	EtCN	Me ₂ AlN: CEtMe	160°–170°	150
Me ₃ Al	<i>tert</i> -BuCN	Me ₂ AlN: C- <i>tert</i> -BuMe	150°	150
Me ₃ Al	PhCN	Me ₂ AlN: CPhMe	160°–170°	177
Me ₂ AlCl	MeCN	ClMeAlN: CMe ₂	160°–165°	150
Me ₂ AlCl	<i>tert</i> -BuCN	ClMeAlN: C- <i>tert</i> -BuMe	240°	150
Me ₂ AlCl	PhCN	ClMeAlN: CPhMe	170°–180°	177
MeAlCl ₂	PhCN	Cl ₂ AlN: CPhMe	170°	228, 229
Et ₃ Al	MeCN	Et ₂ AlN: CMeEt	110°–130°	150
Ph ₃ Al	MeCN	Ph ₂ AlN: CMePh	190°–200°	150
Ph ₃ Al	<i>tert</i> -BuCN	Ph ₂ AlN: C- <i>tert</i> -BuPh	170°	150
Ph ₃ Al	PhCN	Ph ₂ AlN: CPh ₂	130°–150°	97, 177
Me ₃ SnNMe ₂	PhCN	Me ₃ SnN: CPhNMe ₂	25°	95, 155
Ph ₃ PbOMe	CCl ₃ CN	Ph ₃ PbN: C(OMe)CCl ₃	25°	79b
(Ph ₃ Pb) ₂ O	CCl ₃ CN	Ph ₃ PbN: C(OPbPh ₃)CCl ₃	25°	79b

^a All the Al compounds are dimeric.^b Temperatures in Centigrade degrees.

TABLE VIII
ISONITRILE INSERTION REACTIONS

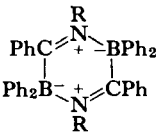
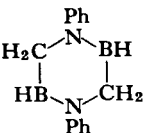
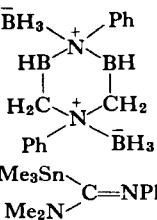
Reactants		Products	Experimental conditions ^a	References
MX _n	RNC			
Me ₃ B	Me ₃ CNC	$\text{Me}_2\text{BCMe}=\text{NCMe}_3 \xrightarrow{20^\circ\text{C}}$ $\begin{array}{c} \text{Me}_2 \\ \\ \text{Me}_3\text{CN}=\text{C}=\text{BMe} \\ \quad \quad \\ \text{MeB} \quad \quad \text{NCMe}_3 \\ \\ \text{C} \\ \\ \text{Me}_2 \end{array}$	<p>−190°–(−60°);</p> <p>20°</p>	55, 56
Et ₃ B	EtNC	$\begin{array}{c} \text{Et} \\ \\ \text{CH}_3\text{CH}=\text{C}=\text{NH}^+-\text{BEt}_2 \\ \quad \quad \\ \text{Et}_2\text{B} \quad \quad \text{C}=\text{CHCH}_3 \\ \\ \text{NH}^+ \\ \\ \text{Et} \end{array}$ $\begin{array}{c} \text{Et} \\ \\ \text{EtC}=\text{N}^+-\text{BEt}_2 \\ \quad \quad \\ \text{Et}_2\text{B} \quad \quad \text{N}^+=\text{CEt} \\ \\ \text{Et} \end{array}$	20°	38
R ₃ B R = Me, Et, Bu	PhNC	$\begin{array}{c} \text{Ph} \\ \\ \text{RC}=\text{N}^+-\text{BR}_2 \\ \quad \quad \\ \text{R}_2\text{B} \quad \quad \text{N}^+=\text{CR} \\ \\ \text{Ph} \end{array} \xrightarrow{200^\circ\text{C}} \begin{array}{c} \text{Ph} \\ \\ \text{R}_2\text{C}-\text{N}-\text{BR} \\ \quad \quad \\ \text{RB} \quad \quad \text{N}-\text{CR}_2 \\ \\ \text{Ph} \end{array}$	20°; 200°	131, 132

TABLE VIII—*continued*

300

M. F. LAPPERT and B. PROKAI

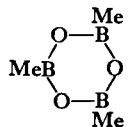
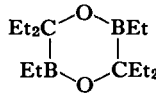
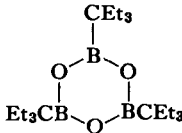
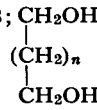
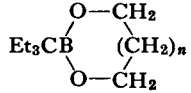
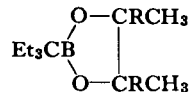
Reactants		Products	Experimental conditions ^a	References
MX _n	RNC			
Et ₃ B	PhNC	<p>The reaction shows a 1,2,3,4-tetraethyl-1,2,3,4-tetraphenylborazane derivative (a cage-like structure with two boron and two nitrogen atoms, each substituted with two ethyl and two phenyl groups) reacting at 300°C to form a 1,2,3,4-tetraethyl-1,2,3,4-tetraphenylborazane derivative (a cage-like structure with two boron and two nitrogen atoms, each substituted with one ethyl and one phenyl group).</p>	180°; 300°	55
Bu ₃ B	C ₆ H ₁₁ NC	<p>The structure shows a 1,2,3,4-tetra(n-butyl)-1,2,3,4-tetra(nonyl)borazane derivative, where the boron atoms are substituted with two n-butyl groups each, and the nitrogen atoms are substituted with one n-butyl and one nonyl group each.</p>	20°	132
Ph ₃ B	C ₆ H ₁₁ NC	<p>The structure shows a 1,2,3,4-tetra(phenyl)-1,2,3,4-tetra(nonyl)borazane derivative, where the boron atoms are substituted with two phenyl groups each, and the nitrogen atoms are substituted with one phenyl and one nonyl group each.</p>	150°	133
Ph ₃ B	PhNC	<p>The structure shows a 1,2,3,4-tetra(phenyl)-1,2,3,4-tetra(phenyl)borazane derivative, where the boron atoms are substituted with two phenyl groups each, and the nitrogen atoms are substituted with one phenyl group each.</p>	80°–90°	133

Ph_3B	RNC $\text{R} = p\text{-Et}_2\text{NC}_6\text{H}_4$		110°	133
$\text{B}_{10}\text{H}_{14}^b$	EtNC	$\text{EtH}_2\text{N}^+ [\text{CB}_{10}\text{H}_{12}]^-$	25°	146
B_2H_6^b	PhNC		0°	265
$\text{Et}_3\text{SnNMe}_2$	PhNC		20°	96

^a Temperatures in Centigrade degrees.

^b As these are hydroboration reactions they should strictly not be included; on the other hand they are the only two examples thus far reported.

TABLE IX
CARBON MONOXIDE INSERTION REACTIONS

Reactants	Products	Experimental conditions ^a	References
(H ₃ B) ₂		25°; THF; trace NaBH ₄	235a
Et ₃ B	(Et ₃ BCO) ₂ , (EtBCO) ₃ ^b	12°-18°; 93 atm	241
Et ₃ B; H ₂ O		52°; 700 atm	139
Et ₃ B; H ₂ O		150°; 950 atm	139
Et ₃ B;  <i>n</i> = 0, 1, 2, or 3		150°; 800 atm	138
Et ₃ B; CH ₃ (CROH)CH ₃ R = H or Me		150°; 800 atm	138

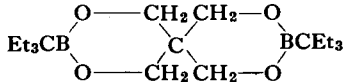
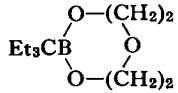
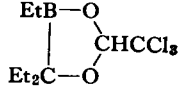
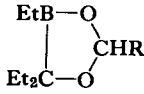
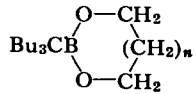
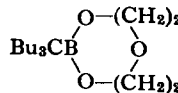
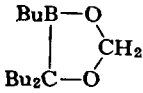
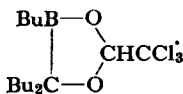
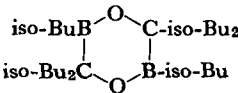
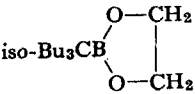
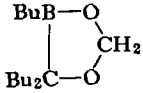
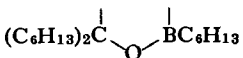
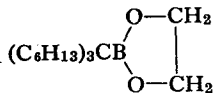
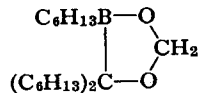
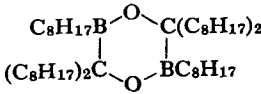
Et_3B ; $\text{C}(\text{CH}_2\text{OH})_4$		150° ; 800 atm	138
Et_3B ; $[\text{CH}_2(\text{OH})\text{CH}_2]_2\text{O}$		150° ; 800 atm	138
Et_3B ; $\text{CCl}_3\text{CH}(\text{OH})_2$		50° ; 700 atm	140
Et_3B ; RCHO $\text{R} = \text{H}, \text{CH}_2\text{Cl}, \text{Me}, \text{Pr}$		50° ; 700 atm ($\text{R} = \text{Me}$) 35° – 55° ; 200 atm	140 241
Pr_3B	$(\text{Pr}_3\text{BCO})_3^b$	150° ; 200 atm	241
Bu_3B ; H_2O	$(\text{Bu}_3\text{CBO})_3$	150° ; 700 atm	139
Bu_3B ; $\text{HOCH}_2(\text{CH}_2)_n\text{CH}_2\text{OH}$ $n = 0$ or 1		150° ; 800 atm	138
Bu_3B ; $[\text{CH}_2(\text{OH})\text{CH}_2]_2\text{O}$		150° ; 800 atm	138

TABLE IX—*continued*

Reactants	Products	Experimental conditions ^a	References
Bu ₃ B; HCHO		50°; 600 atm	140
Bu ₃ B; CCl ₃ CH(OH) ₂		50°; 600 atm	140
iso-Bu ₃ B; H ₂ O		75°; 500 atm	140
iso-Bu ₃ B; (CH ₂ OH) ₂		150°; 800 atm	138
iso-Bu ₃ B; HCHO		50°; 700 atm	140

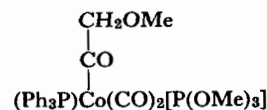
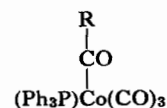
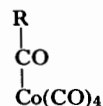
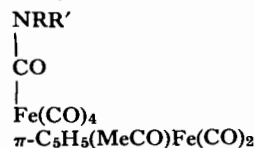
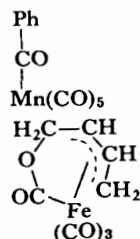
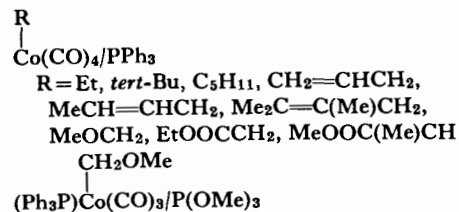
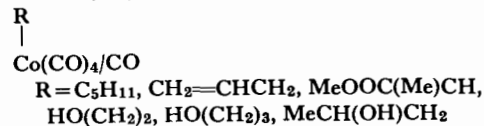
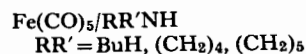
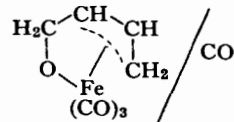
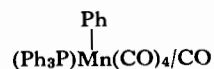
$(n\text{-C}_6\text{H}_{13})_3\text{B}$; H_2O		50°; 900 atm	139
	$[(\text{C}_6\text{H}_{13})_3\text{CBO}]_3$	150°; 900 atm	
$(n\text{-C}_6\text{H}_{13})_3\text{B}$; $(\text{CH}_2\text{OH})_2$		150°; 800 atm	138
$(n\text{-C}_6\text{H}_{13})_3\text{B}$; HCHO		150°; 800 atm	138
$(\text{C}_6\text{H}_{11})_3\text{B}$	$[(\text{C}_6\text{H}_{11})_3\text{BCO}]_2$, $(\text{C}_6\text{H}_{11})_3\text{BCO}^b$	20–22°; 140–175 atm	241
$(n\text{-C}_8\text{H}_{17})_3\text{B}$; H_2O		50°; 900 atm	139
$(\text{PhCH}_2)_3\text{B}$	$[(\text{C}_8\text{H}_{17})_3\text{CBO}]_3$	150°; 900 atm	
$(\text{PhCH}_2\text{CH}_2)_3\text{B}$	$[(\text{PhCH}_2)_3\text{BCO}]_2^b$		241
$\text{MePdCl}(\text{PEt}_3)_2$	$[(\text{PhCH}_2\text{CH}_2)_3\text{BCO}]_2$, $[(\text{PhCH}_2\text{CH}_2)_3\text{BCO}]_n$	150–200 atm	241
$\text{MePdBr}(\text{PEt}_3)_2$	$\text{ClPd}(\text{COMe})(\text{PEt}_3)_2$	25°	32
$\text{MePdI}(\text{PEt}_3)_2$	$\text{BrPd}(\text{COMe})(\text{PEt}_3)_2$	25°	32
$\text{MePtCl}(\text{PEt}_3)_2$	$\text{IPd}(\text{COMe})(\text{PEt}_3)_2$	25°	32
$\text{MePtBr}(\text{PEt}_3)_2$	$\text{ClPt}(\text{COMe})(\text{PEt}_3)_2$	90°; 50–100 atm	32
$\text{MePtI}(\text{PEt}_3)_2$	$\text{BrPt}(\text{COMe})(\text{PEt}_3)_2$	90°; 50–100 atm	32
$\text{PhPtCl}(\text{PEt}_3)_2$	$\text{IPt}(\text{COMe})(\text{PEt}_3)_2$	90°; 50–100 atm	32
$\text{PhPtBr}(\text{PEt}_3)_2$	$\text{ClPt}(\text{COPh})(\text{PEt}_3)_2$	90°; 50–100 atm	32
$\text{PhPtI}(\text{PEt}_3)_2$	$\text{BrPt}(\text{COPh})(\text{PEt}_3)_2$	90°; 50–100 atm	32
	$\text{IPt}(\text{COPh})(\text{PEt}_3)_2$	90°; 50–100 atm	32

^a Temperatures in Centigrade degrees.

^b A structure was not proposed.

TABLE X
INTRAMOLECULAR CARBON MONOXIDE INSERTION REACTIONS

Reactants	Products	Experimental conditions ^a	References
$\pi\text{-C}_5\text{H}_5\text{Mo(CO)}_3\text{Et/CO}$ $\text{W(CO)}_6/\text{LiR}$	$\pi\text{-C}_5\text{H}_5\text{Mo(CO)}_3\text{COEt}$ $\left[\begin{array}{c} \text{R} \\ \\ \text{CO} \\ \\ \text{W(CO)}_5 \end{array} \right]^-$	20°/160 atm	186a 88
Me $\text{Mn(CO)}_5/\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 (= \text{LL})$	CH_3 CO $(\text{LL})\text{Mn(CO)}_4$ or Me CO $\text{Mn(CO)}_3(\text{LL})_2$	25°	185
Me $\text{Mn(CO)}_5/\text{L}$ $\text{L} = \text{CO}, ^b \text{C}_6\text{H}_{11}\text{NH}_2, \text{C}_6\text{H}_{11}\text{NHMe}, \text{PhNH}_2, \text{I}^-,$ $\text{NH}_3, \text{PPh}_3, \text{P(OPh)}_3, \text{P(OCH}_2)_3\text{CCH}_3, \text{AsPh}_3,$ SbPh_3	Me CO LMn(CO)_4	—	9, 47, 48, 48a, 48b, 48c, 65, 66, 111b, 160, 183, 184
Ph $\text{Mn(CO)}_5/\text{C}_6\text{H}_{11}\text{NH}_2$	Ph CO $(\text{C}_6\text{H}_{11}\text{NH}_2)_2\text{Mn(CO)}_4$	20°	160



20°/200 atm

9

0°

126

—

82b

Heat ; pressure

66

0°

121, 127a, 128,
129, 263, 264

0°

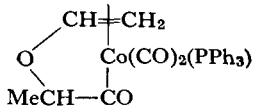
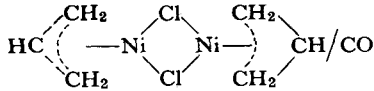
119a, 127, 127a,
128, 129

0°

120

TABLE X—continued

Reactants	Products	Experimental conditions ^a	References
$\begin{array}{c} \text{Me} \\ \\ \text{Co}(\text{CO})_4/\text{L} \\ \text{L} = \text{PPh}_3, \text{P}(\text{OMe})_3, \text{P}(\text{OCH}_2)_3\text{CEt} \end{array}$	$\begin{array}{c} \text{Me} \\ \\ \text{CO} \\ \\ \text{LCo}(\text{CO})_3 \end{array}$	0°	120, 129
	or $\begin{array}{c} \text{Me} \\ \\ \text{CO} \\ \\ \text{L}_2\text{Co}(\text{CO})_2 \end{array}$	70°–75°	120
$\begin{array}{c} \text{Me} \\ \\ \text{L}_2\text{Co}(\text{CO})_2/\text{L} \\ \text{L} = \text{P}(\text{C}_6\text{H}_4\text{OMe-}p)_3, \text{P}(\text{OMe})_3, \\ \text{P}(\text{OCH}_2)_3\text{CEt} \end{array}$	$\begin{array}{c} \text{Me} \\ \\ \text{CO} \\ \\ \text{LCo}(\text{CO})_3 \end{array}$	20°–100°	120
$\begin{array}{c} \text{Me} \\ \\ \text{Co}(\text{CO})_4/\text{EtC}\equiv\text{CEt} \end{array}$	$\begin{array}{c} \text{O} \\ // \\ \text{EtC} - \text{C} - \text{O} \\ \quad \quad \\ \text{EtC} \quad \quad \text{CMe} \\ \\ \text{Co}(\text{CO})_3 \end{array}$	0°	125
$[\pi\text{-C}_3\text{H}_5\text{Co}(\text{CO})_2\text{C}_3\text{F}_7]^+[\text{ClO}_4]^-/\text{HF or NaF}$	$\pi\text{-C}_3\text{H}_5\text{Co}(\text{COC}_3\text{F}_7)\text{X}$	—	266a
$\begin{array}{c} \text{H}_2\text{C} - \text{CO} \\ \quad \\ \text{OC} \quad \text{OEt} \\ \diagdown \quad / \\ \text{Co}(\text{CO})_3/\text{EtC}\equiv\text{CEt} \end{array}$	$\begin{array}{c} \text{O} \\ // \\ \text{EtC} - \text{C} - \text{O} \\ \quad \quad \\ \text{EtC} \quad \quad \text{CCH}_2\text{CO}_2\text{Et} \\ \\ \text{Co}(\text{CO})_3 \end{array}$	0°	125

$\text{HCo(CO)}_4/\text{CH}_2=\text{CHOCH}=\text{CH}_2 + \text{PPh}_3$		0°	122
	$\text{CH}_2=\text{CHCH}_2\text{CONiCl(CO)}_2$	0°	121a
$\text{C}_8\text{H}_{17}\text{Pt(CO)Cl/PPh}_3$	$(\text{Ph}_3\text{P})_2\text{Pt(COC}_8\text{H}_{17})\text{Cl}$	20°	288c

^a Temperatures in Centigrade degrees.

^b Also $\text{RMn(CO)}_5 \xrightarrow[\text{R=Me, Et, Pr (65, 66)}]{\text{Heat; pressure}} \text{RCOMn(CO)}_5$.

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Olefin Oxidation with Palladium(II) Catalyst in Solution

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I. Introduction	321
A. History and Industrial Applications	321
B. The Scope of the Reaction	323
II. Metal-Olefin Complexes	324
A. Palladium-Olefin Complexes as Reaction Intermediates	324
B. The Structure of Olefin Complexes and the Nature of the Metal- Olefin Bond	326
III. The Reaction in Aqueous Solutions	328
A. Palladium(II) Species in Solution	328
B. Kinetics of the Olefin Oxidation	329
C. Experiments with D ₂ O and with C ₂ D ₄	330
D. The Mechanism of the Ethylene Oxidation.	330
E. The Reaction in the Presence of Copper(II) Salts	339
IV. The Reaction in Nonaqueous Solvents	343
A. Experimental Results	343
B. The Reaction Mechanism	346
References	349

I

INTRODUCTION

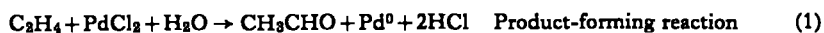
A. History and Industrial Applications

Until 1960, aldehydes and ketones were commercially synthesized from olefins mainly by a two-step reaction. The olefins were hydrated to alcohols with subsequent dehydrogenation or oxidation of the alcohol to the corresponding carbonyl compound. The direct oxidation of olefins with oxygen to carbonyl compounds was a significant technological achievement of Dr. Smidt and co-workers (32, 66, 67) of the Consortium für elektrochemische Industrie, a research company of Wacker Chemie.

Smidt and his associates were passing mixtures of ethylene and oxygen over palladium on carbon carriers with the hope of making ethylene oxide.

They found instead that some acetaldehyde was obtained especially when water and hydrochloric acid were accidentally present as a consequence of the catalyst preparation. The activity of the catalyst decreased rapidly and the palladium (which was originally distributed uniformly on the support) eventually formed a shiny deposit on the surface. They further observed that addition of cupric chloride or ferric chloride favored the formation of acetaldehyde. The experiments suggested that some of the elementary palladium was dissolved by the acid in the presence of oxygen and that palladium chloride was the oxidant. Cupric chloride and ferric chloride oxidize palladium metal much faster than does oxygen in the presence of acid. The cuprous chloride and ferrous chloride readily react with oxygen to give back the cupric and ferric salts. This was the explanation for the beneficial effect of cupric chloride and ferric chloride. Further experimentation showed that it was more satisfactory to carry out the reactions with the catalyst salts in water solutions than to use heterogeneous catalysts. Several noble metals were tried but the rates were significantly lower than with palladium. Cupric chloride was preferred over ferric chloride and other oxidants mainly because the reoxidation of cuprous chloride with oxygen is a very fast reaction.

The above process can be represented schematically by the following reactions:



The three reactions [Eqs. (1)–(3)] have been known individually for more than sixty years (66). The achievement was to combine them into a workable process. In the process the palladium salts are required only in very small concentration and the copper(II) salts are continuously regenerated with oxygen. Direct oxidation of ethylene with oxygen takes place, producing acetaldehyde in almost quantitative yields [overall Eq. (4)].

The Wacker process for acetaldehyde has been industrialized on an extensive scale (68). The process can be carried out either in one or two stages. In the one-stage process, ethylene and oxygen are passed together through an aqueous solution of the palladium and cupric salts and all the reactions occur simultaneously. In the two-stage process, ethylene is totally consumed in an aqueous solution of the palladium and cupric salts

by the reactions represented by Eqs. (1) and (2). After separation of the product acetaldehyde, the reduced catalyst is oxidized with air by the reaction represented in Eq. (3). The chemistry of both processes is essentially the same as far as the main reaction is concerned. Major differences are only in technology and by-product formation.

The feasibility of using similar reactions for the commercial production of acetone from propylene and methyl ethyl ketone from butenes has also been demonstrated (43, 68).

The success of the Wacker process encouraged several laboratories to study the reactions in nonaqueous solvents. It was established that in acetic acid solutions vinyl esters could be made while in alcohol, vinyl ethers and acetals were produced (54, 71). The combination of the ethylene oxidation in acetic acid with the reoxidation reactions lead to the development of a new process for the production of vinyl acetate (29, 38). This process is being used on a commercial scale by two companies, Celanese Chemical Company in the United States and Imperial Chemical Industries in the United Kingdom.

B. The Scope of the Reaction

1. Aqueous Solutions

The application of the reaction to olefins other than ethylene has been discussed in detail by Smidt *et al.* (66). All monoolefins with at least one hydrogen atom on both carbon atoms of the double bond react to give the corresponding ketone. The carbonyl group appears on that carbon atom to which the anion would add in ionic additions of acids (Markownikoff's rule). When using high molecular weight olefins (hexene or larger) the yield is, however, low and the product is contaminated with other ketone isomers (22). This is probably due to isomerization of the olefin (23, 24, 34, 35, 69). Diolefins, like 1,3-butadiene, react under mild conditions to give unsaturated aldehydes and under more drastic conditions to give the corresponding ketoaldehydes. Cyclic olefins, alkyl-aryl olefins and unsaturated carboxylic acids behave like aliphatic compounds. Palladium salts catalyze the hydrolysis of vinyl esters and chlorides (66, 67). Clement and Selwitz (22) have improved the laboratory preparation of methyl ketones with palladium chloride and α -olefins by using aqueous dimethylformamide as a solvent.

2. *Nonaqueous Solvents*

The reaction in nonaqueous solvents has been presented as a general vinylation reaction (71) but it is much more complicated than this. The majority of the published work has been done in acetic acid and we will refer specifically to this solvent.

Ethylene oxidation yields vinyl acetate, acetaldehyde, ethylidene diacetate, and ethylene glycol acetates (38, 53, 54). Propylene yields isopropenyl acetate, propenyl acetate, small amounts of allyl acetate (51, 70, 71), and a yellow crystalline compound, $C_6H_{11}PdCl$, called by Moiseev *et al.* (52), π -hexenylpalladium complex. When oxidizing higher α -olefins (hexene or higher) the main products seem to be the corresponding allyl esters (80). As an example, 1-hexene yields 68% of the acetate of 2-hexen-1-ol. Also with higher olefins the reaction can be complicated by the simultaneous isomerization of the olefin (23, 24, 34, 35, 69).

II

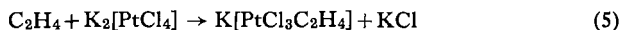
METAL-OLEFIN COMPLEXES

A. *Palladium-Olefin Complexes as Reaction Intermediates*

The first olefin complex of a platinum group metal to be discovered was Zeise's salt [$K(PtCl_3C_2H_4)$] in 1830 (15). For over a hundred years after its discovery there was little further progress in this field, until the work of Kharasch and Anderson in the 1930's (15). These olefin complexes have, however, been the subject of intensive study during the past decade (6, 31) with the result that large numbers of these compounds are known, the structures of many are understood, and applications for them are now being discovered (32, 43, 66, 67, 68).

The oxidation of ethylene to acetaldehyde by the platinum group metals has been known since 1894 (66). The palladium-ethylene complex which is postulated as an intermediate cannot be isolated in water solutions due to the high rate of decomposition by water. However, a dimeric species [$PdCl_2C_2H_4$]₂ was prepared in nonaqueous solvent by Kharasch *et al.* (40). This complex is a yellow substance which decomposes rapidly in water with production of acetaldehyde, elementary palladium, and hydrochloric acid. The analogous platinum complex or the monomeric Zeise's salt are much

more stable. Zeise's salt can be prepared in cold water (66) by direct reaction of ethylene with potassium tetrachloroplatinate.

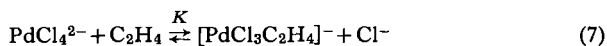


If this compound is heated with water, it decomposes into acetaldehyde, elementary platinum, potassium chloride, and hydrochloric acid (1).



More direct evidence of the formation of an olefin-palladium(II) complex, as a reactive intermediate in the olefin oxidation in water solutions, was obtained recently. In one study (56), π -complex formation between olefin and palladium chloride was detected in aqueous solutions under conditions of high acid and chloride concentrations. Henry (36), while studying the kinetics of the ethylene oxidation in water with palladium salts, observed that the reaction showed an initial rapid ethylene uptake, followed by a slower ethylene absorption. The volume of ethylene initially taken up exceeded that required to saturate the solution with ethylene. This volume taken up in excess of the solubility requirements was found to be unaffected by acid concentration but decreased as the chloride ion concentration increased. It was concluded that the formation of an ethylene-palladium chloride complex is the first step in the reaction. Similar results were obtained using propylene, 1-butene, and *cis*- and *trans*-2-butene (37). Pestrikov and Moiseev (60), in studying the reaction of 1-butene with palladium chloride solutions in water, obtained evidence of the formation of two complexes: $[\text{PdCl}_3\text{C}_4\text{H}_8]^-$ and $[\text{PdCl}_2(\text{H}_2\text{O})\text{C}_4\text{H}_8]$.

All the evidence mentioned above indicates that in any mechanism for the olefin oxidation using palladium catalyst in water solutions the first step must be the formation of an olefin-palladium(II) complex by replacement of one of the ligands of the palladium(II) ion by the olefin. As it is known that substitution reactions of palladium(II) ion in water are very fast (3), this reaction and the reverse one should be fast, with the equilibrium rapidly established. With free chloride concentrations of over 0.2 mole/liter, the predominant palladium(II) species in solution is PdCl_4^{2-} (see Section III, A). The reaction may then be presented for ethylene as follows:



$$K = \frac{[\text{PdCl}_3\text{C}_2\text{H}_4]^- [\text{Cl}^-]}{[\text{PdCl}_4^{2-}] [\text{C}_2\text{H}_4]} \quad (8)$$

Smidt and co-workers (66) observed that solutions of palladium chloride in nonaqueous solvents also absorbed olefins readily. The volume of olefin absorbed exceeded that required to saturate the solution with the olefin and was dependent on the palladium chloride concentration. The solutions of ethylene and palladium chloride in acetic acid precipitate palladium metal after addition of sodium acetate (54). Simultaneously, ethylene is oxidized to vinyl acetate. The complex $[\text{PdCl}_2\text{C}_2\text{H}_4]_2$ prepared by the method of Kharasch (40), reacts with sodium acetate solutions in acetic acid in the same way (54). These experiments indicate that in nonaqueous solvents also the first step in the olefin oxidation is the formation of an olefin-palladium(II) complex.

B. The Structure of Olefin Complexes and the Nature of the Metal-Olefin Bond

Many physical methods have been used to study the nature of olefin-metal complexes. Infrared and nuclear magnetic resonance spectroscopy and X-ray crystallography have all been fruitfully applied. The structure of monoolefin, platinum, and palladium complexes in the solid state is illustrated in Fig. 1. In Zeise's salt and in the related simple ethylene complexes of platinum and palladium, the axis of the carbon-carbon double bond is normal to the plane in which the metal atom and halogen lies (31, 45). The carbon-carbon double bond is largely unchanged, but is apparently weakened by the coordination; the bond becomes longer and the C=C vibration frequency in the infrared ($\sim 1500\text{ cm}^{-1}$) is lowered. The frequency shift ranges from 60 to 150 wave numbers. Proton magnetic resonance studies (45) are consistent with a planar configuration of the hydrogen atoms of the ethylene molecule, the interproton vector of each methylene group being parallel to the Cl—Pt—Cl line. An accurate estimate of the interhydrogen distances in the molecule cannot be made (due to apparent rotational oscillations of the coordinated ethylene¹) although it seems to be little distorted from its ground-state configuration in the gas. This spatial arrangement of the atoms has been determined in $[\text{PtCl}_3\text{C}_2\text{H}_4]^-$

¹ Nuclear magnetic resonance spectrum of $\pi\text{-C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$ indicates that in this compound coordinated ethylene molecules rotate with the coordination bond as axis (22a). The low energy barrier to rotation suggests that both dxz and dxy metal orbitals could participate in the π bond.

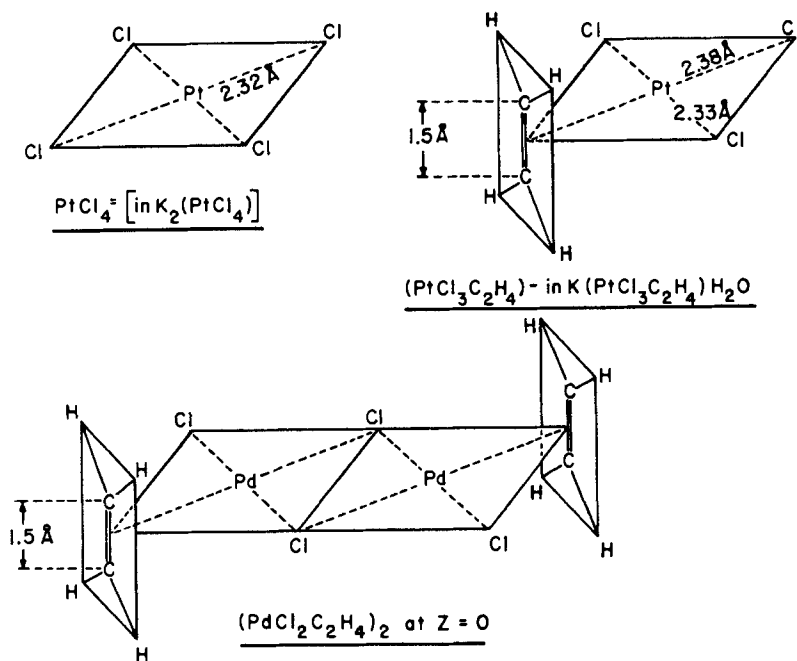


FIG. 1. The structure of metal-olefin complexes.

and other olefin-platinum complexes, and in $[\text{PdCl}_2\text{C}_2\text{H}_4]_2$ and $[\text{PdCl}_2\text{styrene}]^2$. Values of the different bond lengths have been reviewed (2).

None of the theories proposed before 1951 to explain the nature of the bonding in metal-olefin complexes was entirely satisfactory. The work of

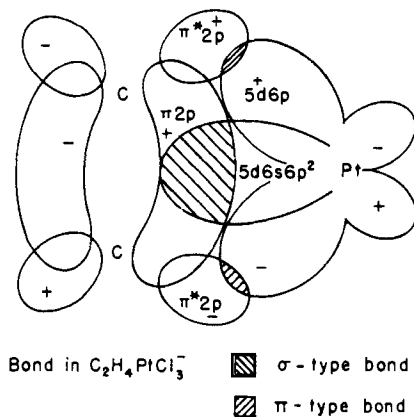


FIG. 2. The presumed nature of the bond in metal-olefin complexes.

Dewar and Chatt allowed the description of the bond as it is now generally accepted. Ethylene acts as a donor molecule contributing two of its electrons (from the $\pi_{\text{C}_2\text{H}_4} 2p$ molecular orbital) into a vacant dsp^2 hybrid orbital of the metal ion, forming a σ -type bond. At the same time the central metal atom "back-donates" electrons from its filled d or dp hybrid into the vacant antibonding $\pi_{\text{C}_2\text{H}_4}^* 2p$ molecular orbital of the olefin forming a π -type bond. This back-donation of electrons from the metal atom leaves the olefin much less charged than if it were acting purely as a two-electron donor. A representation of this bond is presented in Fig. 2.

III

THE REACTION IN AQUEOUS SOLUTIONS

A. Palladium(II) Species in Solution

Aqueous solutions of palladium(II) in the presence of chlorides have been studied by several investigators using mainly spectrophotometric methods (7-9, 26, 30, 64, 65, 72, 75, 82). No binuclear chloro complexes seem to exist in aqueous solution (82). The predominant ionic species below pH 2 and at different chloride concentrations are Pd^{2+} , PdCl^+ ,

TABLE I

FORMATION CONSTANTS OF CHLORO COMPLEXES OF Pd(II) IN WATER SOLUTION^a

Reference	Conditions	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	$\log K$
82	$T=25^\circ\text{C}$, $\mu=1.0$, $[\text{H}^+]=1.0$	4.4	3.34	2.34	1.38	11.46
7	$T=25^\circ\text{C}$, $\mu=0$	6.0	4.60	2.5	2.0	15.1
64	$T=20^\circ\text{C}$, $\mu=0.8$, $[\text{H}^+]=0.6$	4.34	3.54	2.68	1.68	12.24
65	$T=30^\circ\text{C}$	—	—	—	—	12.57
9	$T=25^\circ\text{C}$	3.88	3.06	2.14	1.34	10.40
26	$T=21^\circ\text{C}$, $\mu=0.44$, $[\text{H}^+]=0.21$	6.2	4.7	2.5	2.6	16.0
	29.5°C	6.0	4.5	2.4	2.6	—
	38.0°C	5.9	4.1	2.2	2.5	—
30		—	—	—	—	12.2 ± 0.5
44	$T=25^\circ\text{C}$	—	—	—	—	12.3
75	$T=25^\circ\text{C}$, $\mu=4.0$, $[\text{H}^+]=4.0$	—	—	—	—	13.3

^a $K_n = [\text{PdCl}_n^{2-n}]/[\text{Cl}^-][\text{PdCl}_{n-1}^{2-(n-1)}]$; $K = [\text{PdCl}_4^{2-}]/[\text{Pd}^{2+}][\text{Cl}^-]^4$; T , temperature; μ , ionic strength.

PdCl_2 , PdCl_3^- , and PdCl_4^{2-} , in which the coordination number four of palladium(II) is satisfied by water molecules. The proportion of each of the species will depend, of course, on the free chloride concentration and can be calculated with the values of the consecutive formation constants of the chloro complexes. The values of the consecutive and cumulative formation constants determined by different authors are given in Table I. The results of different investigators differ somewhat, but for our purposes the differences are not very important. The majority of the kinetic experiments in the study of the ethylene oxidation have been made at free chloride concentrations higher than 0.2 mole/liter. Calculations using any of the sets of stability constants lead to the same general conclusion: The predominant species in the presence of 0.2 mole/liter of free chloride (or higher chloride concentration) is the tetrachloro complex.

B. Kinetics of the Olefin Oxidation

Kinetics experiments related to the olefin oxidation have been carried out by several investigators. Smidt and co-workers (66, 67) found that the reaction rate increases with palladium(II) and C_2H_4 concentration and that the reaction is inhibited by Cl^- and H_3O^+ . Joy and Orchin (39) proved that ethyl alcohol is not an intermediate in the oxidation and this has been confirmed (32). The reaction was found to be first order in palladium(II) and C_2H_4 (36, 76, 79, 81). In the absence of chloride ion, the reaction was reported to be second order in palladium(II) (79). The proton inhibition is first order (36, 79) while the rate depends on the inverse square of the chloride ion concentration (36, 76, 81). Increasing the ionic strength (μ), increases the rate up to a value of $\mu = 0.4$. Further increases in ionic strength decrease the rate (36). Propylene, 1-butene, and *cis*- and *trans*-2-butene obeyed the same rate expression (25, 37). Surprisingly, cyclohexene oxidation did not show proton inhibition (78).

All these experimental data were obtained in systems in which either no oxidant was present or *p*-benzoquinone was used as the oxidant. In this way the complicating effect of cupric and cuprous salts in changing the free chloride concentration was avoided. Some kinetic studies have been reported, however, in the presence of cupric and cuprous salt (25, 46-48, 50, 67). These studies will be commented on in Section III, E, 3.

As a conclusion from all the kinetics experiments (related to the oxidation

of olefins by aqueous solutions of palladium salts in the presence of chloride ion) the following kinetic equation seems to be firmly established for ethylene, propylene, 1-butene, and *cis*- and *trans*-2-butene.

$$-\frac{d[\text{C}_2\text{H}_4]}{dt} = k \frac{[\text{PdCl}_4^{2-}][\text{C}_2\text{H}_4]}{[\text{Cl}^-]^2[\text{H}_3\text{O}^+]} \quad (9)$$

C. Experiments in D_2O and with C_2D_4

When ethylene was oxidized with palladium(II) salts in D_2O , no deuterium was incorporated in the acetaldehyde molecule (67). As all the hydrogen atoms of the acetaldehyde molecule came from ethylene, in one of the reaction steps a hydrogen shift must occur. An isotope effect $k_{\text{H}}/k_{\text{D}}$ of 4.05 was also observed in D_2O (55).

If the reaction is run in water but using deuterated ethylene (C_2D_4) only a small isotope effect is found (36): $k_{\text{H}}/k_{\text{D}} = 1.07$. The result indicates that no carbon-hydrogen bond is broken during the rate-determining step.

The experimental data summarized so far lead to the following conclusions for ethylene oxidation by PdCl_2 :

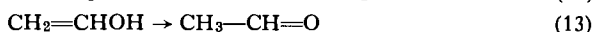
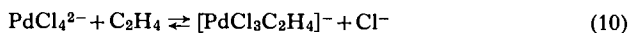
1. The main palladium(II) ionic species in water solutions at free chloride concentrations higher than 0.2 molar (pH below 2) is PdCl_4^{2-} .
2. An ethylene-palladium complex is one of the reactive intermediates.
3. Ethyl alcohol is not an intermediate in the acetaldehyde production.
4. All the hydrogens of the acetaldehyde molecule come from ethylene.
5. No carbon-hydrogen bond is broken during the rate-determining step.
6. The rate of ethylene oxidation decreases with increasing ionic strengths for values above 0.4.
7. When using D_2O as the solvent, the isotope effect $k_{\text{H}}/k_{\text{D}}$ is 4.05.
8. The kinetics of the reaction follows the expression

$$-\frac{d[\text{C}_2\text{H}_4]}{dt} = k \frac{[\text{PdCl}_4^{2-}][\text{C}_2\text{H}_4]}{[\text{Cl}^-]^2[\text{H}_3\text{O}^+]} \quad (9)$$

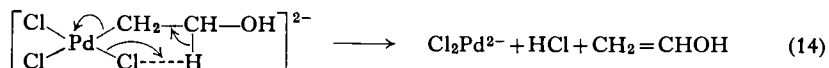
D. The Mechanism of the Ethylene Oxidation

Several mechanisms have been proposed for the ethylene oxidation. Moiseev *et al.* (54), based on the reactions of the ethylene palladium

chloride complex with acetic acid (vinyl acetate is produced) and alcohols (acetals are produced) proposed the following reaction scheme:



The decomposition of the σ -bonded complex $[\text{CH}_2\text{OH}-\text{CH}_2\text{PdCl}_3]^{2-}$ was represented as



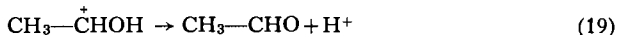
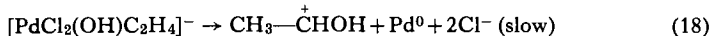
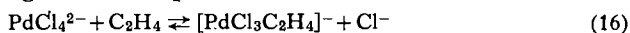
This reaction scheme necessarily leads to a kinetic expression in which the chloride inhibition will be first order and no proton inhibition will be shown.

$$-\frac{d[\text{C}_2\text{H}_4]}{dt} = K \frac{[\text{PdCl}_4^{2-}][\text{C}_2\text{H}_4]}{[\text{Cl}^-]} \quad (15)$$

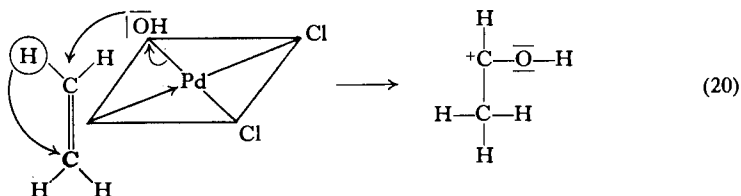
Also, a proton of the water would enter the acetaldehyde molecule. All these deductions from the proposed mechanism are in disagreement with the experimental data. The mechanism has, however, two interesting features:

1. the proposition that water instead of hydroxyl ion is the attacking species;
2. the postulation of a σ -bonded complex $[\text{CH}_2\text{OH}-\text{CH}_2\text{PdCl}_3]^{2-}$ as an intermediate between the π complex and the decomposition reaction.

Smidt and his co-workers (67), based on the experiments with D_2O , proposed the following reaction sequence:



It can be readily shown that the kinetic equation derived with this mechanism is similar to the experimental one. The slow step, Eq. (18), was represented as follows:



The mechanism also explains why no deuterium enters the acetaldehyde molecule in a D_2O reaction solvent. The isotope effect in D_2O can be explained by a change in the ionization constant of H_2O (85)

$$K_{H_2O}/K_{D_2O} = 5 \quad (21)$$

The main objection is that the mechanism shows a breaking of a hydrogen-carbon bond in the rate-determining step which cannot be reconciled with the low deuterium isotope effect obtained with C_2D_4 . The hydroxyl attack on the complex can also be criticized in view of its small concentration in the reaction medium. Henry (36) has shown that the rate of ethylene oxidation can be expressed by the relationship

$$-\frac{d[C_2H_4]}{dt} = 2 \times 10^{-4} \frac{[PdCl_3C_2H_4]^-}{[Cl^-][H_3O^+]} \quad (22)$$

using the value of 17.4 for the formation constant of the complex $[PdCl_3C_2H_4]^-$ from $PdCl_4^{2-}$ and ethylene. The rate of attack by hydroxyl ion has to be greater than the rate of oxidation if that attack is not the rate-determining step. Accordingly, we can write

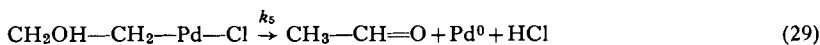
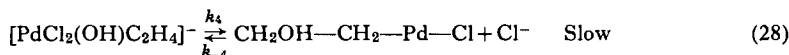
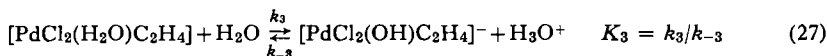
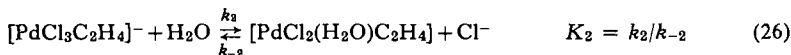
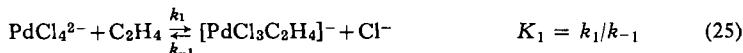
$$k[PdCl_3C_2H_4]^- [OH^-] > 2 \times 10^{-4} \frac{[PdCl_3C_2H_4]^-}{[Cl^-][H_3O^+]} \quad (23)$$

$$kK_w > 2 \times 10^{-4} \frac{1}{[Cl^-]} \quad (24)$$

where k is the specific rate constant of the reaction of $[C_2H_4PdCl_3]^-$ with OH^- and for a $[Cl^-]$ of 2×10^{-1} , $k > 10^{11}$ mole $^{-1}$ liter sec $^{-1}$. This means that to be consistent with the experimental data the specific constant of the reaction of hydroxyl ion with the olefin-palladium complex ion should be higher than 10^{11} mole $^{-1}$ liter sec $^{-1}$, which seems to be unlikely. The fastest diffusion-controlled process in solution has a k of that order ($H_3O^+ + OH^- \rightarrow 2H_2O$, $k = 1.3 \times 10^{11}$) and one would expect lower values for reaction between ions of equal sign and lower mobilities (28).

Dozono and Shiba (25) have proposed a mechanism for propylene oxidation which is similar to that of Smidt *et al.* (67). It does not account for the low deuterium isotope effect when the oxidation is run with deuterated olefins.

In 1964, Henry (36) presented a mechanism for the reaction in which many of the ideas previously proposed are included. *The mechanism accounts for all the experimental data.* According to this proposal the reaction proceeds through the following steps:



$$-\frac{d[\text{C}_2\text{H}_4]}{dt} = k_4 K_1 K_2 K_3 \frac{[\text{PdCl}_4^{2-}][\text{C}_2\text{H}_4]}{[\text{Cl}^-]^2 [\text{H}_3\text{O}^+]} \quad (30)$$

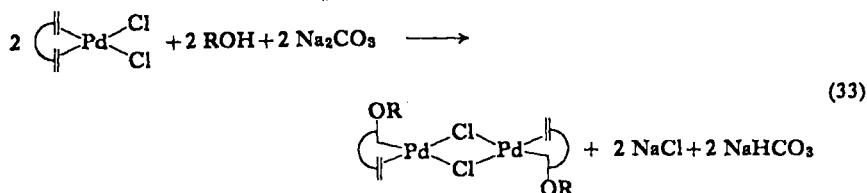
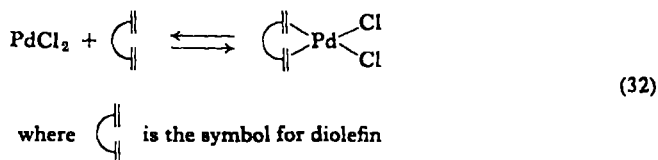
which is of the form of the experimental expression. Henry measured K_1 and made an estimation of K_2 and K_3 . His values are $K_1 = 17.4$, $K_2 \cong 10^{-3}$ mole l^{-1} , and $K_3 \cong 10^{-6}$ mole l^{-1} . The product $k_4 K_2 K_3$ was measured experimentally as 2×10^{-4} mole² l^{-2} sec⁻¹ and with this and the estimated values of K_2 and K_3 the value of k_4 was estimated in 10^{-5} sec⁻¹. Also determined were the energy and entropy of activation from the plot of $\log k^1 = f(T)$ where $k^1 = k_4 K_2 K_3$. The values are $\Delta H^\ddagger = 19.8$ and $\Delta S^\ddagger = -8.7$ eu. If one assumes that K_2 and K_3 do not change with temperature, the determined value of ΔH^\ddagger is the one which corresponds to the energy of activation of the reaction represented by Eq. (28). One can calculate the value of ΔS^\ddagger for this reaction as 31 eu at 25° C.

The first two steps in Henry's mechanism, Eqs. (25)–(26), are also accepted by other authors (76, 81) and account for the marked chloride inhibition of the reaction. Equation (27) accounts for the proton inhibition, and the deuterium isotope effect of the reaction in D_2O . The effect will be due to a decrease in the ionization constant of the hydrated complex (a weak acid) in D_2O (63).

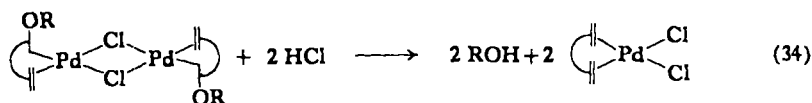
$$\frac{K_3[\text{H}_2\text{O}]}{K_3[\text{D}_2\text{O}]} = \frac{K_1[\text{PdCl}_2(\text{H}_2\text{O})\text{C}_2\text{H}_4]}{K_1[\text{PdCl}_2(\text{D}_2\text{O})\text{C}_2\text{H}_4]} \cong 3.5 \quad (31)$$

The hydroxo complex in Eq. (27) could also be formed by reaction of the aquo complex with hydroxyl ion. However, Henry (36) has calculated that the specific rate constant for a hydroxyl attack should be higher than 10^{14} mole⁻¹ liter sec⁻¹, which is much higher than the fastest diffusion-controlled process in solution. Equation (28), transformation of the π complex into a σ complex, is introduced by the author to account for the low deuterium isotope effect of the reaction when using C_2D_4 . If the π complex decomposed directly into products, this step would be (to account for the kinetics) the rate-determining process and the hydride shift (rupture of the carbon-

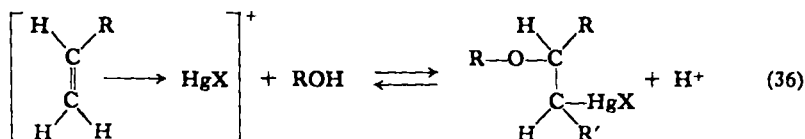
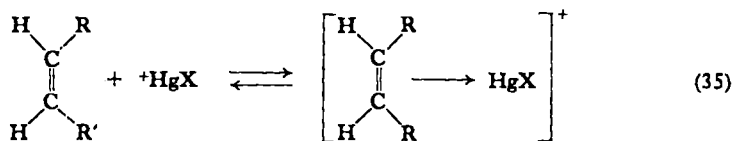
hydrogen bond) should take place during this step. This would produce, in contradiction with the experimental results, a primary isotope effect. Transformation of a π to a σ complex has been proposed by other authors (33, 54, 57, 81). Also, one can find justification for the proposal of such a σ intermediate in the chemistry of platinum and palladium olefin complexes. The transformation of a π complex into a σ complex is known for Pd and Pt diolefin complexes (19, 20).



where the Pd atom is σ -bonded to the C atom of the methylene group. The σ complex can be reversed to the π complex by addition of hydrochloric acid.



These reactions strongly resemble the ones observed with Hg^{2+} olefin complexes (14).



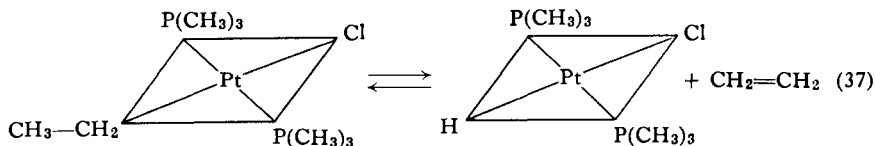
No σ -bonded complexes of palladium chloride and monoolefins have been isolated. This must be due to the instability of the alkyl derivatives when chloride is the only additional ligand coordinated to the metal atom.

In the alkyl derivatives obtained with diolefins, the σ -bonded compound is stabilized by the presence of the other double bond coordinated to the same palladium atom. It is well known that certain ligands stabilize the alkyl platinum and palladium compounds (16). The ligands that give the best stabilization are those which cause electron pairing in the resulting complex molecule like cyclopentadienyl anion, carbon monoxide, tertiary phosphines, and tertiary arsines. A series of stable compounds has been prepared having the formula and structure illustrated below (16):



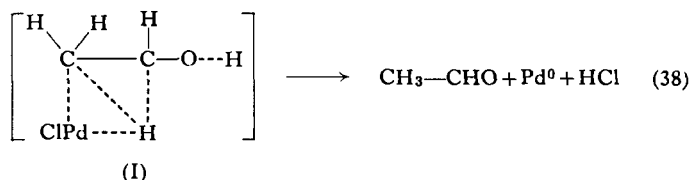
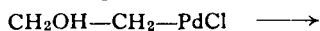
where X is a halide and R' is an alkyl group.

Even with these stabilizing ligands, palladium alkyls with β hydrogens are much more unstable than the corresponding Pt compounds (11). These instabilities may be related to the tendency of the central atom to labilize the hydrogens in the β position. As an example, platinum alkyls reversibly eliminate olefin with formation of a hydride (18).



The major instability of the Pd analog could be explained by the instability of the palladium hydride (17) which drives the equilibrium to the side of decomposition.

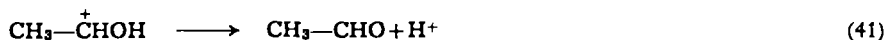
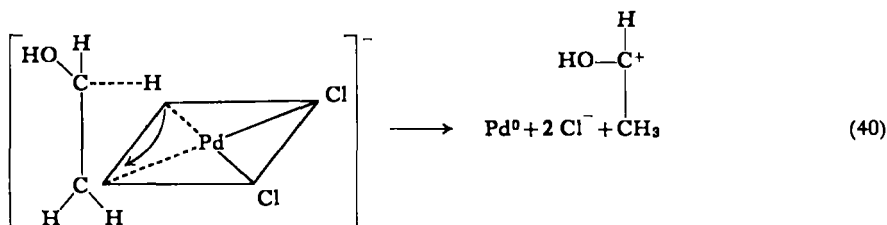
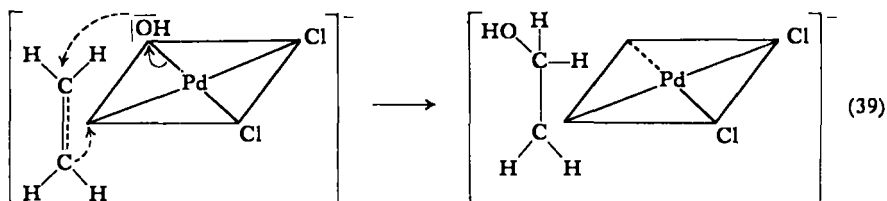
This labilization of β hydrogens could be one reason why palladium is a better catalyst than platinum in the olefin oxidation.² The decomposition of the σ -bonded compound, Eq. (29), is visualized by Henry (36) in the following way:



² Another explanation could be the fact that while palladium complexes are substitution labile, platinum complexes are inert. This would make the first two steps slow reactions.

The activated complex (I) is formed in which palladium assists the hydride shift as it leaves with its electrons.

The formulation of the two-coordinated σ complex by Henry can be criticized because the usual coordination number of palladium is four. We prefer to visualize the reactions, Eqs. (28)–(29), in the following way:

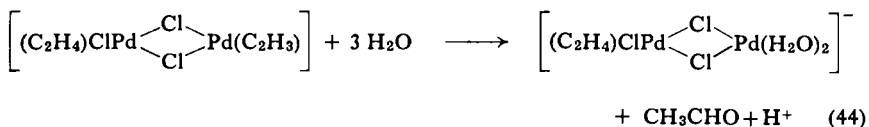
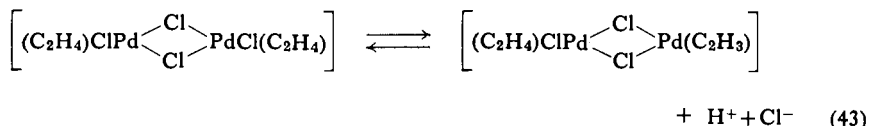
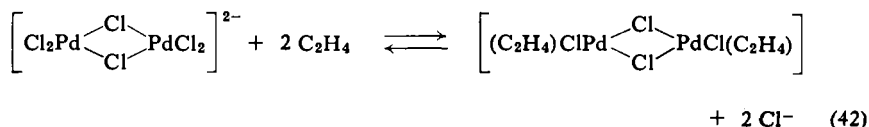


Rotation of ethylene with the coordination bond as axis (Section II, B) could facilitate the ligand migration step represented in Eq. (39). The intermediate carbonium ion in Eq. (41) has been suggested by Smidt and co-workers (67). In Eq. (39) a three-coordinated intermediate does not necessarily exist, for the fourth coordination position could be occupied by the solvent.² This last formulation is used by Henry (37) in studying the mechanism of oxidation of higher olefins, which is similar to the one proposed for ethylene. The formation constants of the π complexes and the reaction rates were measured. It was concluded that the insertion reaction (ligand migration) or transformation of the π -bonded complex into the σ -bonded complex has little carbonium ion character in the transition state. A concerted four-center addition for the rate-determining oxypalladation step of the oxidation was proposed.

Moiseev, Vargaftik, and Syrkin, after a series of papers on kinetics of ethylene oxidation (54–56, 79, 81), published an article (57) in which they suggested a mechanism which is essentially the same as the one proposed by Henry (36). The same sequence of reactions is presented, but they stated

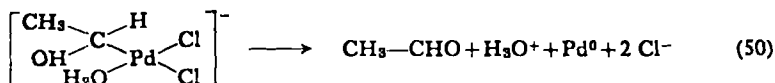
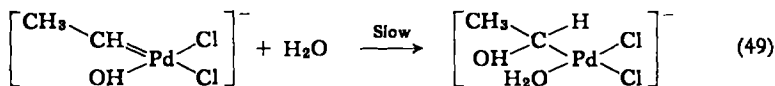
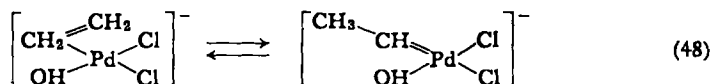
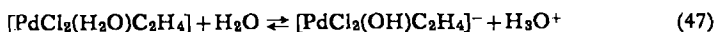
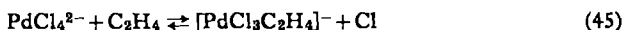
that equilibrium is not established in the first two steps (formation of the ethylene palladium complex and exchange of one of the chloride ligands by water). This was concluded from a comparison of the observed and predicted rate of reaction at different palladium(II) concentrations. In the calculation of the reaction rate the authors used the values of K_1 and K_2 [Eqs. (25)–(26)] they have previously published (56). It is possible that these values are in error (specifically K_2 , which seems too high), as indicated by Henry (36).

Some authors have proposed palladium(II) dimers as reactive intermediates (46, 47).

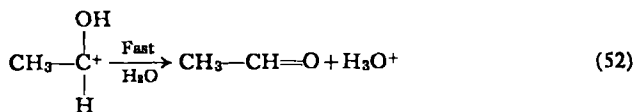
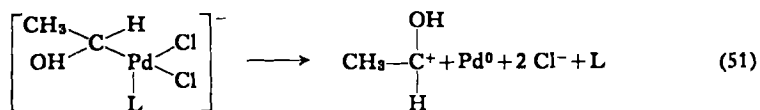


To account for the first-order dependence on palladium(II) the authors postulate that the predominant palladium(II) species in aqueous solutions is the dimer, which has been proved to be incorrect (82). In the equilibrium presented in Eq. (43) ethylene loses a proton, which leaves the complex with one of the coordinated chloride ions. This type of reaction has been shown only with higher olefins where one of the protons in the α position to the double bond is the one that leaves the molecule and a π -allyl complex is formed. With such an intermediate one hydrogen atom of the acetaldehyde molecule would also come from water, which is in contradiction to the experiments in D_2O . In Eq. (44) the formation of a zero-valent palladium complex is postulated. This complex can precipitate palladium metal or can be reoxidized to the +2 stage in the presence of a suitable oxidant. Independently of the particular formulation of the zero-valent palladium complex, the proposition is in a way justified as some stable zero-valent compounds of palladium are known (27, 41, 73). In a later paper the same authors propose PdCl_2^{2-} as the transient zero-valent intermediate (48).

Finally, to explain some experimental results obtained by Davies (23) when isomerizing olefins, a carbene-type intermediate has been proposed by Chatt (13). If such an intermediate were accepted, one could think of a sequence of reactions as follows:



This reaction sequence will also account for all the experimental data if we assume the reaction represented in Eq. (49) as the rate-determining step. Also Eq. (50) could represent the rate-determining step if the σ -bonded intermediate were decomposed into a carbonium ion in a slow step followed by a fast reaction.



If we compare this with Henry's mechanism we can see that the main differences are the introduction of a new step in which a carbene-type intermediate is proposed, and that the organometallic compound formed from that intermediate carries the OH group on the carbon bonded to the palladium. We believe that at the present state of knowledge Henry's mechanism is to be preferred. It is the simplest one that explains all the experimental data in water solutions. In addition, there is already evidence

of the transformation of palladium(II) π complexes into σ -bonded organo-metallic compounds, some of which have been isolated. Such evidence is lacking in the case of the carbene intermediate.

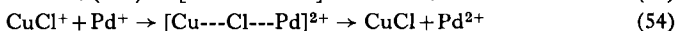
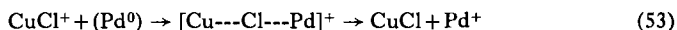
E. The Reaction in the Presence of Copper(II) Salts

1. The Reoxidation of Palladium

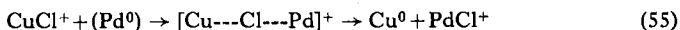
Cupric chloro complexes are unstable (49) and in the catalyst solution the concentration of Cu^{2+} and CuCl^+ may be significant although some CuCl_2 and CuCl_3^- may be present.

It is well known that elementary palladium can be dissolved in hydrochloric acid solutions in the presence of oxygen. The reaction, however, is very slow. On the other hand, dissolution of palladium metal by cupric halide solutions is fast and, as the cuprous salts formed can be easily re-oxidized with oxygen, the use of cupric salts allows the zero-valent palladium to be oxidized with oxygen with a high overall reaction rate.

The normal potential of palladium is reduced in the presence of chlorides, due to the formation of chloro complexes. The potential of the $\text{Cu(II)}-\text{Cu(I)}$ couple is raised at the same time (44). One of the effects of the chloride ion in the system is thus a thermodynamic one, i.e., more favorable oxidation potentials are achieved. It is possible that there is also a kinetic effect; the chloride ion may increase the rate of dissolution of elementary palladium by copper(II) salts. A bridged activated complex could be formed, the reaction rate being high due to the effectiveness of chloride as an electron mediator (74). The reaction could occur either with palladium metal or with a short-life intermediate complex of palladium(0) and it may be produced in two steps:

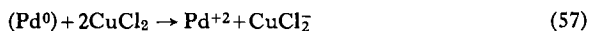


or



The ionic species in the equations presented above could be any of those previously discussed. The symbol (Pd^0) represents palladium metal or a chloride complex of Pd^0 .

As the mechanism of the reaction is now known [no kinetic data for palladium(0) oxidation have been found] we will represent it with the general equation



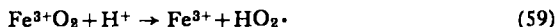
2. The Oxidation of Copper(I) with Oxygen

The oxidation of copper(I) and iron(II) by molecular oxygen is believed to proceed through similar mechanisms. As the iron(II) oxidation has been more thoroughly investigated a very brief discussion of this reaction is pertinent.

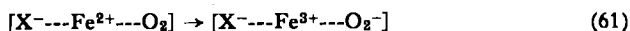
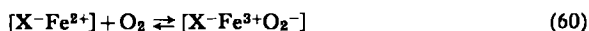
One of the first mechanisms for the iron(II) oxidation was formulated by Weiss in 1934 and since then the same author has revised it in several publications (83, 84). The Weiss mechanism proposes as a primary process the formation of an iron-oxygen ion-pair complex.



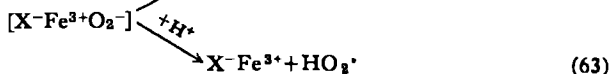
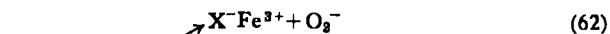
The complex will break up slowly to produce the radical ion O_2^- (or the radical $\text{HO}_2\cdot$)



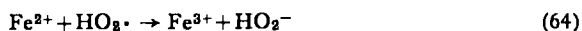
The increase in rate produced by anions such as F^- , $\text{P}_2\text{O}_7^{4-}$, H_2PO_4^- is due to the stabilization of the transition state by the anion



where X is the stabilizing anion. The new complex may eventually break up either directly or by interaction with protons.

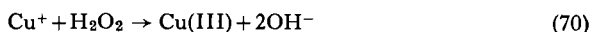
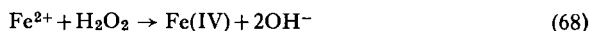


After this reaction, a series of fast steps follows

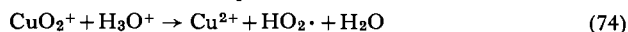
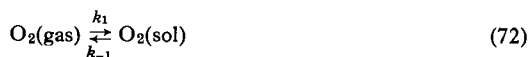


All the kinetic data, especially the kinetics of iron(II) oxidation with copper(II) as catalyst, fit very well into the Weiss free radical mechanism. This, plus the indicated existence in solution of these short-lived free radical intermediates (61, 77), gives good support to the free radical picture of the reaction. However, other reaction paths have been mentioned. The formation of intermediates of iron and copper with unfamiliar oxidation

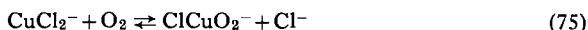
states has been postulated by Cahill and Taube (10) in the reaction of hydrogen peroxide with copper(I) and iron(II)



The kinetics of copper(I) oxidation with oxygen has been studied only under certain conditions (12, 59). The reaction is so fast that the experiments have to be done at very low copper(I) concentrations. The rate of oxidation is proportional to the copper(I) and oxygen concentration. The reciprocal of the rate is a linear function of the reciprocal of the hydrogen ion concentration. The following mechanism was proposed by Nord (59):



followed by a sequence of fast steps in which three more cuprous ions per oxygen molecule are oxidized. Nord (59) did not elaborate in detail the nature of the fast steps but mentioned the species $\text{HO}_2\cdot$, H_2O_2 , and $\cdot\text{OH}$ as intermediates, which could fit in reactions similar to the ones represented in Eqs. (64)–(67). As chloride ion inhibits the reaction Nord (14) suggested that Eq. (73) could also be represented as



The first order kinetics in copper(I) were established in very dilute solutions and it is possible that at higher copper(I) concentrations a reaction path second order in copper(I) is operative. This second-order reaction in the reduced metal ion has been observed in the iron(II) oxidation (83).

3. *Pseudo-Catalysis by Copper(II)*

The mechanism of the product formation reaction, palladium reoxidation, and copper(I) reoxidation with oxygen have been discussed up to this point as independent reactions. We will now discuss the situation if all the reactions occur simultaneously. The most simple assumption will be that the reactions will proceed following the same mechanism as when they occur independently. This assumption can be tested by a study of the

products and kinetics of the overall reaction. If the assumption is correct, the product of the overall reaction should be mainly acetaldehyde. The kinetics of the reaction should show the same responses to changes in catalyst composition and conditions as one would predict from the kinetics of each of the particular systems studied. The first of these conditions is fulfilled; acetaldehyde is by far the predominant ethylene oxidation product under various conditions. The second of these conditions is more difficult to establish quantitatively. The concentration of the "free" ions (especially the chloride ion) is not known exactly due to the uncertainty in the values of the dissociation constants of the complex ionic species in solution. Qualitatively, however, the changes in the overall reaction rate are the ones that one would expect from the kinetic equations previously presented [Eq. (9)]. When the overall reaction was run under conditions in which no accumulation of cuprous salts and elementary palladium occurs (25, 46-48, 50, 67) the rate was proportional to the palladium concentration and ethylene pressure. Proton and chloride inhibition were also noticed.

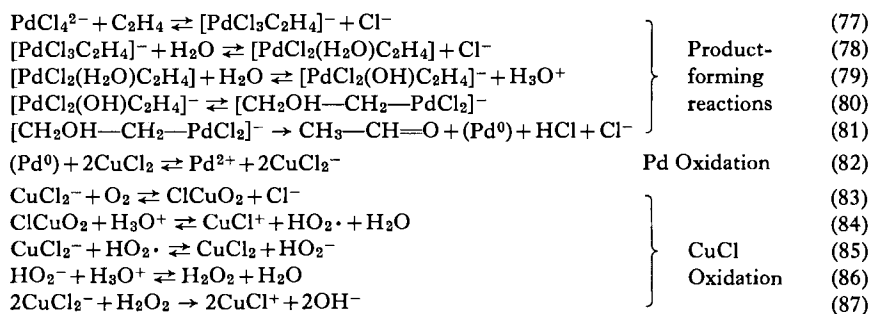
Matveev *et al.* (48) reported that the reaction rate increased with increasing copper(II) concentration

$$\text{Rate} = K_1 + K_2 [\text{Cu(II)}]^2 \quad (76)$$

The authors interpreted the results as a proof of two different reaction paths, one which is copper(II)-independent and predominates at low copper(II) concentrations, and the other, catalyzed by copper(II), which involves a palladium(II)-copper(II) complex. We do not believe, however, that true copper(II) catalysis is operative in the Wacker reaction. The experiments were performed by adding copper(II) to a solution in which the total chloride was kept constant. They disregarded the decreasing free chloride concentration (which is the one that enters into the kinetic equation) by formation of copper(II) chloro complexes. Since the chloride ion inhibits the reaction, the addition of copper(II) increased the reaction rate due to the decrease in free chloride. The net effect was one of pseudo-catalysis by copper(II). One can demonstrate that if an approximate correction to free chloride is made no catalysis by copper(II) seems to exist. This correction can be made by using the values of the stability constants of the copper(II) chloro complexes (49). Moreover, Dozono and Shiba (25), found that the oxidation of propylene with palladium(II)-copper(II) catalyst follows the same kinetics established by Henry (36) in the ethylene oxidation in the absence of copper(II) and determined that the reaction was zero order in

copper(II) (25). The authors did not correct the chloride concentration to free chloride but as the copper(II) concentration was low, the effect of this cation was not significant.

In conclusion, we can say that with the available experimental data *the existence of a copper(II)–palladium(II) reaction path has not been proved in water* and it is satisfactory to assume that when all the reactions occur simultaneously (as in a one-stage system) the mechanism proposed for each of the individual reactions is still valid. Accordingly, the complete series of kinetic steps could be represented as follows:



The reactions represented in Eqs. (82) and (87) are not single kinetic steps but overall fast reactions, the mechanisms of which are in doubt, as was discussed previously. The dotted lines used in the arrows of some of the back-reactions indicate that during normal operating conditions the equilibrium in these reactions is not established. The mechanism for the copper(I) oxidation was proposed only for very dilute solutions of copper(I). It is possible that at higher copper(I) concentrations a reaction path second order in copper(I) is also operative (see Section III, E, 2).

IV

THE REACTION IN NONAQUEOUS SOLVENTS

A. Experimental Results

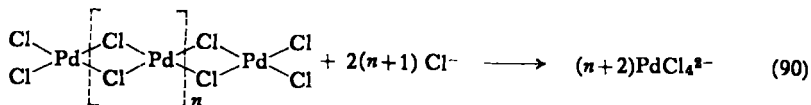
1. Reactions in Alcohols

Very few studies have been published related to olefin oxidation in non-aqueous solvents. The scope of the reaction was briefly discussed in Section I, B, 2. We will preferentially refer here to the reaction of the lower olefins, especially ethylene.

The complex $[\text{PdCl}_2\text{C}_2\text{H}_4]_2$ prepared by the method of Kharasch *et al.* (40), reacts readily with alcohols to produce the corresponding diacetals of acetaldehyde (54) and small amounts of vinyl ethers.



The same products are obtained if ethylene reacts with palladium(II) chloride solutions in alcohols (54). Soluble chlorides, i.e., lithium chloride, are added to solubilize the polymeric palladium(II) chloride.



When ethylene was oxidized with palladium(II) salts in CH_3OD , practically no deuterium was incorporated in the acetaldehyde dimethyl acetal product (53). Thus, the majority of the acetals are not made by addition of the alcohol to the vinyl ether, and in some of the steps of the acetal formation a hydride shift must occur.

2. The Reactions in Acetic Acid

Ethylene is readily absorbed by solutions of palladium chloride in acetic acid, but palladium metal is not precipitated (66), indicating that oxidation–reduction has not taken place. Only when some soluble acetate is added (sodium or lithium acetate) does precipitation of palladium metal and oxidation of ethylene to vinyl acetate, ethylidene diacetate, and acetaldehyde take place (53, 54).



When ethylene was oxidized with palladium(II) salts in CH_3COOD , practically no deuterium was incorporated in the ethylidene diacetate product (53). Thus the majority of ethylidene diacetate is not made by addition of acetic acid to vinyl acetate, and in some of the steps of the formation of ethylidene diacetate a hydride shift must occur.

Acetaldehyde may be produced through different routes. The ethylene–palladium complex can react with the water present in the solvent. Also, vinyl acetate can be hydrolyzed, especially in the presence of palladium(II)

(67). Even in the complete absence of water, vinyl acetate can produce acetaldehyde and acetic anhydride by a reaction catalyzed by palladium(II) and acetate ion (21).

In addition to the products mentioned above, acetic acid solutions of palladium chloride and certain oxidants, i.e., copper(II) salts, give good yields of ethylene glycol acetates, especially if the ratio of chloride ion to acetate ion is high (38).



In this reaction reduction of palladium(II) to palladium metal has been indicated. However as the reaction has only been reported in the presence of copper(II) or other oxidants, it is possible that a direct reduction of the oxidant occurs, and no change in the oxidation state of palladium(II) is produced.

The kinetics of the ethylene oxidation in acetic acid in the presence of sodium acetate has been studied using palladium(II) acetate (4). The reaction is first order in ethylene and palladium(II).

The effect of ethylene pressure is surprising; increasing the ethylene pressure increases the proportion of vinyl acetate and decreases ethylidene diacetate (38).

Some experiments using deuterated propylene have been reported by Stern (70). The overall acetate ester yield based on palladium(II) was 15% and 10% when using propylene and propylene-2-*d*, respectively. The product distribution was equal for both isotopic species of propylene: about 64% of propenyl acetate and 36% of isopropenyl acetate. The rate of oxidation of propylene was greater than that of propylene-2-*d* by a factor of 2.8. The degree of deuterium retention in the acetate product was 75%. From the isotope effect it was concluded that a C—H bond was broken during the rate-determining step. According to the author the extent of deuterium retention supports a mechanism involving a 1,2-shift of hydride from the attacked carbon, followed by proton loss from an adjacent carbon atom. With this picture, and assuming the absence of an appreciable isotope effect in the latter step the author calculated a minimum deuterium retention of 71%.

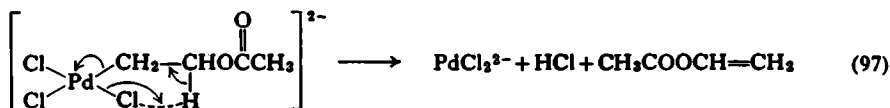
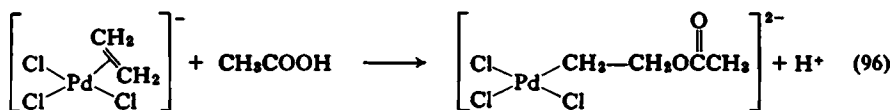
Stern's picture implies that the hydride shift is produced in the rate-determining step (to account for the deuterium isotope effect) while the subsequent loss of a proton from the adjacent carbon atom is not. If this

were true, the rate of formation of the isopropenyl acetate should be significantly lower with propylene-2-*d* than with untagged propylene. On the other hand, the rate of formation of propenyl acetate should be the same in both cases. This was not observed, however, for the product distribution was practically the same in both the tagged and untagged experiments. Another complicating factor is the possibility of isomerization of the olefin catalyzed by palladium(II) (23, 24, 34, 35, 69). In experiments using deuterated olefins (23) the data are consistent with a stepwise migration of hydrogen atoms from one carbon to the next only. This isomerization could be at least partially responsible for the high deuterium retention. However, the high isotope effect is difficult to explain if we assume that all the retention is due to isomerization. In conclusion there is some indication of a hydride shift in the mechanism of vinyl ester formation, but more experiments should be done to confirm this conclusion. Probably the hydride shift and the loss of a proton from adjacent carbon is a concerted reaction. This could explain why the product distribution is the same in the experiments with propylene and propylene-2-*d*.

B. The Reaction Mechanism

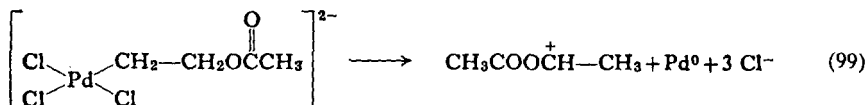
The palladium(II) species in solution are not known and a detailed kinetic study of all the reactions has not been published. Therefore, the sequence of reaction steps is not known. The products are probably made through decomposition of a π - or σ -bonded complex.

Moiseev *et al.* (54), proposed the following picture of the oxidation in acetic acid:



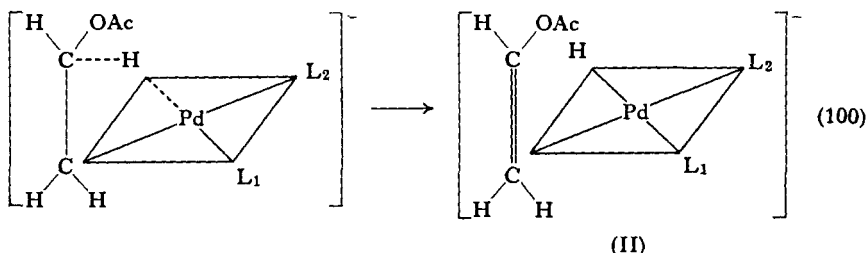
in which a σ -bonded complex is formed by attack with acetic acid while sodium acetate assisted in the removal of the proton. The σ -bonded complex

will decompose as indicated in Eq. (97), producing vinyl acetate. Ethylidene diacetate will be produced by addition of acetic acid to the vinyl acetate. Further experiments by Moiseev *et al.* (53) show this to be incorrect. Instead, they propose the formation of a carbonium ion intermediate from the decomposition of the σ -bonded complex.

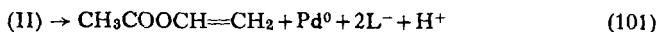


The authors did not elaborate on the mode of decomposition of the complex. The carbonium ion intermediate could lose a proton and make vinyl acetate or react with the solvent and make ethylidene diacetate. A similar picture was proposed for the reaction in alcohols.

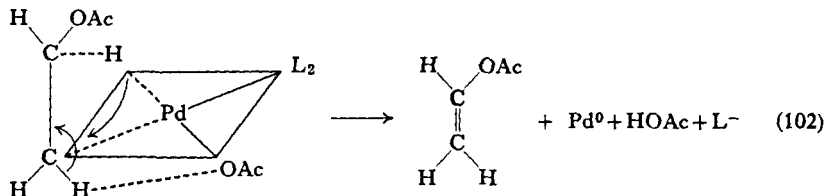
Based on the proposed decomposition in water of the σ -bonded intermediate (Section III, D), the following picture seems attractive:



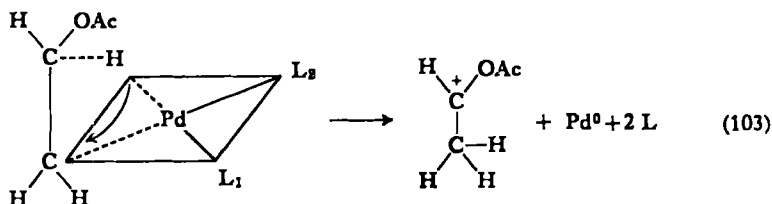
The acetate group has been represented by OAc and the other palladium(II) ligands as L_1 and L_2 . The σ -bonded intermediate loses a hydride to the palladium with formation of the coordinated vinyl ester. The hydride complex (II) will then decompose to palladium metal and the free ester.



Some evidence has been presented for a hydride shift in the mechanism of vinyl ester formation (Section IV, A). Since the above mechanism does not involve a hydride shift the following picture could be considered:

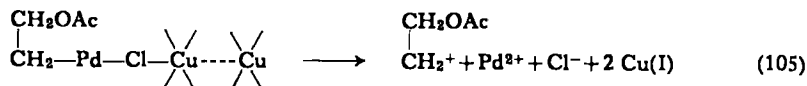
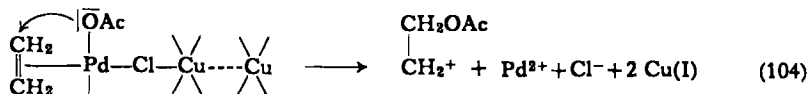


In this picture when L_1 is an acetate group, it assists the removal of a proton from the σ -bonded complex while palladium assists the hydride shift and leaves with its electrons. Equation (102) represents a concerted action of the coordinated palladium(II) ion as electron acceptor with an acetate ligand acting as proton acceptor. This could partially explain the changes in product distribution when the acetate and chloride concentrations are changed (38). Ethylidene diacetate could be made when L_1 is not an acetate ion (probably chloride ion). In this case the hydride shift will be produced as above but the proton will not be removed and a carbonium ion will result.



This carbonium ion will then react with acetate ion to produce ethylidene diacetate.

Finally, when ethylene glycol acetates are made, it seems that the simultaneous presence of palladium(II) and copper(II) is needed and also that the ratio of chloride ion to acetate ion should be high (38). This suggests a palladium(II)-copper(II) complex intermediate. In this complex direct electron transfer to the copper(II) through a chloride bridge could occur. This could be represented by either of the following equations:



The carbonium ion would react with acetate ion and form ethylene glycol diacetate. The copper(II) complex bridged to the palladium(II) could be the acetate dimer, which is known to exist in acetic acid (42). Also, the existence of palladium(II) carboxylate bridged dimeric and trimeric species are known in organic solvents (58, 62). It could be possible that these polymeric species are also important in explaining the changes observed in product distribution in acetic acid when changing the conditions (38, 53).

Finally, regarding olefins other than ethylene, only with propylene have some intermediates been proposed (5). To explain the formation of isopropenyl acetate, *cis*-propenyl acetate, *trans*-propenyl acetate, the corresponding alkylidene diacetates, and small amounts of allyl acetate, the following intermediates were suggested: $\text{ClPdCH}_2\text{CH}_2\text{CH}_2\text{OAc}$, $\text{ClPdCH}_2\text{CHMeOAc}$, and $\text{ClPdCHMeCH}_2\text{OAc}$.

Evidently much more work remains to be done in acetic acid to understand the mechanism of all these reactions. The study of the palladium(II) species in solution in the absence and presence of copper(II) acetates and chlorides, a more detailed kinetic study and more experiments with deuterated olefins are needed.

ACKNOWLEDGMENTS

I am indebted to the Celanese Chemical Company Technical Center for making possible the preparation of this review article. I am grateful to Dr. E. N. Wheeler and Dr. F. Basolo for valuable discussions and suggestions. I appreciate Dr. Wheeler's critical reading of the manuscript.

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Author Index

Numbers in parentheses are reference numbers and indicate that an author's work is referred to although his name is not cited in the text. Numbers in *italic* indicate the page on which the complete reference is listed.

A

- Abbott, R. K., 57(88), *85*
 Abel, E. W., 3(1), 7(6, 14), 8(2, 6, 10, 14),
 9(3), 10(6, 11), 11(6), 12(2, 3, 6, 11),
 13(2, 3, 6, 11), 22(14), 24(2), 25(2, 3),
 26(3), 27(10), 28(2, 8, 11, 15), 29
 (2, 4, 8, 14), 30(6, 11), 31(9, 11),
 32(5, 14), 33(4, 5, 11, 14, 15), 34(14),
 36(15), 37(17, 18), 38(14), 41(2),
 44(16), 46(13), 48(7, 12), 51(1, 2, 4, 6),
 52(6), 54(6, 14), 55(14), 57(7, 14),
 59(14), 60(6, 14), 65(6, 14), 67(1),
 69(3, 7), 70(7), 71(3, 10), 75(10, 11),
 78(11, 14), 82(6), 83(6), *83*
 Abraham, M. H., 251(1, 2), 297(1, 2), *310*
 Abrahams, S. C., 96(1), *131*
 Adams, D. M., 113(2), *131*
 Adams, R., 248(164b), 292(164b), *315*
 Alcock, N. W., 101, 102(3), 103(3),
 125(3), 126(3), *131*
 Alder, R. W., 245(3), *310*
 Alexander, L. C., 116(145), 124(145),
 131(145), *135*
 Allegra, G., 99, 100, 101(123), *131, 132, 134*
 Allerhand, A., 183(59), *221*
 Alleston, D. L., 160(77), 161(77, 86, 88),
 162(77), 165(86), *167*
 Allred, A. L., 3(107), 8(107), 9(107), 19
 (107), 23(107), 24(107), 25(107),
 29(107), 34(107), 35(107), 41(107),
 42(107), 45(19), 51(107), 52(107),
 53(107), 54(107), 59(107), 64(107),
 65(107), 66(107), 67(107), 81(107),
 83, 85, 212(184), *224*
 Almenningen, A., 39(20), 40(20), *83*
 Alpress, C. F., 207(155), *223*
 Anderson, H. H., 9(23), 10(21, 25, 26, 28),
 11(26), 12(26), 25(26), 29(25, 26),
 30(25), 32(25), 35(23, 27, 28), 36(22),
 52(21, 22, 26), 53(26), 54(28), 70(24),
 73(23), 74(25), 83, 84, 158(68), *167*,
 172(9, 10), 187(74), 194(90, 92, 95),
 202(10), 203(95, 132, 133), 207(10,
 132, 133), 208(162, 163, 164, 165, 166),
 209(9, 10, 95, 132, 133, 162, 163, 164,
 165, 166, 170, 171, 172, 173), 211
 (74, 181), 212(9, 10, 74, 132, 163, 164,
 165, 181, 183), 213(95, 132, 133),
 219, 221, 222, 223, *224*
 Anderson, J. S., 325(1), *349*
 Andres, R. J., 204(145, 148), 205(148),
 214(145, 148), *223*
 Andrews, T. D., 129(83, 85), *133*
 Andrianov, K. A., 2(29), 6(30), 76(30), *84*,
 283(292), *319*
 Angel, T. H., 201(120), *222*
 Anker, R. M., 253(3a), *310*
 Antler, M., 50(31), 73(31), *84*
 Aoyama, K., 270(4), *310*
 Armitage, D. A., 7(6), 8(6, 10), 10(6, 11),
 11(6), 12(6, 11), 13(6, 11), 27(10),
 28(8, 11), 29(4, 8), 30(6, 11), 31(9, 11),
 32(5), 33(4, 5, 11), 46(13), 48(7, 12),
 51(4, 6), 51(6), 54(6), 57(7), 60(6),
 65(6), 69(7), 70(7), 71(10), 75(10, 11),
 77(11), 82(6), 83(6), *83*
 Arnold, H. R., *310*
 Atwell, W. H., 240(99, 100, 101), 264(99),
 266(100, 101), *312*
 Austin, J. A., 22(56), 26(56), 81(56), *84*
 Aynsley, E. E., 178(43), 189(43), 218(43),
 220
- ## B
- Backer, H. J., 8(32, 34, 35, 36, 37, 38, 39,
 40, 41), 9(33), 23(36), 25(37), 33(39),
 36(36), 39(33, 34, 40, 118, 119), 64
 (36), 66(32, 34, 37, 38, 40, 41), 67(32,
 34, 35, 39, 41), 68(35, 36), 69(7),
 76(32), 78(32, 39, 41), 80(32, 36),
 81(33), 82(33), *84, 86*
 Baenziger, N. C., 327(2), *349*

- Bailey, M. F., 99(9), 130(7, 8, 9), 131(10), 131
 Bailey, N. A., 101, 112(12, 13), 117(11, 13), 131(12, 13), 131
 Bailey, R. E., 263(279), 319
 Baker, E. B., 249(6), 251(6), 293(6), 297(6), 310
 Baker, H. R., 14(52), 84
 Ballhausen, C. J., 96, 131
 Bankov, Yu. I., 289(232), 317
 Banks, C. K., 204(139, 145), 206(139), 214(139, 145), 223, 271(7), 310
 Bannister, W. D., 242(8, 10), 275(8, 10), 306(9), 307(9), 310
 Barbieri, R., 143(27, 39), 156(27, 65), 157(27), 165, 166, 197(109), 211(177), 222, 224
 Barkie, P. E., 99, 131
 Barror, A. L., 14(194), 56(194), 88
 Basolo, F., 255(183, 184), 256(183), 257(184), 293(272), 306 (183, 184, 185), 315, 318 325(3), 349
 Baudet, M., 283(246), 287(246), 291(246), 317
 Bauer, H., 2(42), 11(42), 74(42), 84
 Bauer, J. H., 186(66), 187(66), 191(66), 192(166), 221
 Baum, S. A., 23(43), 73(43), 84, 162(90), 165(90), 167
 Bauson, H. W., 271(11), 310
 Bayer, O., 278(237), 280(237), 282(237), 287(237), 317
 Bayer, R., 245(82b), 307(82b), 312
 Beach, A. L., 191(88), 221
 Beachell, H. C., 181(51), 182, 183(51), 200(51, 161), 220, 222
 Beattie, I. R., 138, 139, 142(7), 144(7), 149(3), 154(155,7), 165
 Beck, W., 177(36), 179(36, 46), 189(36, 46), 194(36), 208(46), 215(185a), 218(36, 46), 220, 224
 Becke-Goehring, M., 13(44), 51(44), 84
 Becker, E. I., 17(146, 165), 57(165), 70(146, 165), 86, 87
 Becker, M., 216(187), 224
 Beg, M. A. A., 270(12), 310
 Bell, H. C., 272(13), 310
 Belov, A. P., 324(51, 52), 345(4), 349(5), 349, 351
 Bengela, D., 271(243), 272(243), 317
 Bennett, M. A., 324(6), 349
 Bennett, M. J., 97(16, 17), 98(18), 130(18, 19), 131
 Berlin, A. A., 84
 Berndt, A. F., 130(20), 132
 Berthelot, M., 225, 271(14, 15, 16), 310
 Besolova, E. A., 289(89), 312
 Best, L. R., 5(154), 21(154), 72(154), 86
 Beumel, O. F., 15(134), 72(134), 86
 Beverage, A. D., 270(62), 275(62), 311
 Bevilland, P., 11(232), 82(232), 89
 Bey, A. E., 240(279a), 319
 Beyer, H., 278(17), 281(17, 18), 282(17), 287(17), 310
 Bhattacharya, S. N., 217(193a), 224
 Bibler, J. P., 235(19, 288a), 293(19, 288a), 310, 319
 Binger, P., 232(164a), 233(164a), 239(164a), 240(164a), 315
 Birch, S. F., 202(127), 211(127), 222
 Birckenbach, L., 170(1), 219
 Bird, C. W., 233(19a), 254(19a), 310
 Birkofer, L., 16(46), 18(46), 19(46), 22(46), 34(46), 52(46), 69(46), 71(46), 84, 174(26), 200(117, 118), 208(167), 216(26, 117), 220, 222, 223, 295(20), 296(20, 21), 310
 Biryukov, A. A., 328(7, 8), 349
 Bisnette, M. B., 126(105), 134
 Bither, T. A., 174(29), 183(29), 194(29), 202(29), 207(29), 208(29), 220
 Bittner, H., 253(133), 300(133), 301(133), 314
 Blackman, L. C. F., 8(47), 49(47, 48), 51(47, 48), 59(47), 64(47, 48), 66(47, 48), 84
 Bladon, P., 292(22), 310
 Blake, D., 7(49), 8(49), 16(49), 57(49), 84, 139, 143(9), 165
 Block, D. P., 328(26), 350
 Bloemer, A., 270(281), 318
 Bloodworth, A. J., 12(50), 56(50), 84, 232(25, 29), 236(29a), 246(25, 29), 250(25), 278(25, 28), 279(23, 25, 27, 28), 283(23, 24, 25, 26, 28), 284(28, 29a), 285(23, 25, 28, 29a), 288(23), 289(24, 27), 291(24), 296(24), 310
 Blount, J. F., 118(21), 128(53), 132

- Blümcke, A., 23(84), 43(84), 51(84), 85
 Blum, M. S., 50(51), 84
 Boone, J. L., 279(30), 281(30), 286(30), 310
 Boord, C. E., 271(31), 310
 Booth, G., 255(32), 305(32), 310
 Borgstrom, P., 14(53), 84
 Borisov, A. E., 262(211), 271(209, 210), 316
 Boss, C. R., 307(126), 313
 Bost, R. W., 14(52, 53), 84
 Bott, R. W., 249(33, 34), 293(33, 34), 310
 Bottei, R. S., 2(177), 87
 Boulton, A. H., 253(55), 255(55), 299(55),
 300(55), 311
 Brach, O., 159(70), 167
 Bradley, D. C., 248(35), 292(35), 310
 Bradley, H. B., 96(22), 132
 Brady, D. B., 7(6, 14), 8(6, 14), 10(6), 11(6),
 12(6), 13(6), 22(14), 28(15), 29(14),
 30(6), 32(14), 33(14, 15), 34(14), 36
 (15), 37(18), 38(14), 48(7), 51(6),
 52(6), 54(6, 14), 55(14), 57(7, 14),
 59(14), 60(6, 14), 65(6, 14), 70(7),
 77(14), 82(6), 83(6), 83
 Brandstätter, O., 6(237), 41(237), 42(237),
 76(237), 89
 Braye, E. H., 114(89), 117(88), 130(23),
 131(23), 132, 133
 Breederveld, H., 13(54, 55), 51(54, 55),
 60(54), 84, 247(36, 37), 291(36, 37),
 311
 Bresadola, S., 253(38), 299(38), 311
 Breslow, D. S., 255(127, 127a, 128, 129),
 307(127, 127a, 128, 129), 308(129), 314
 Brinckman, F. E., 142(25), 143(25), 165
 Brintzinger, H., 233(38a), 271(39), 311
 Britton, D., 182(52, 53, 55), 184(52), 185
 (53, 55, 62), 199(52, 55), 203(52), 220,
 221
 Brois, S. J., 251(40, 41), 297(41), 311
 Brown, D. A., 114(89), 133
 Brown, H. C., 232(42), 233(42), 255(235a),
 302(235a), 311, 317
 Brown, H. P., 22(56), 26(56), 81(56), 84
 Brown, J. F., 263(43), 311
 Brown, M. P., 8(58), 41(57), 73(57, 58), 84,
 160(73), 167
 Bruce, R., 292(22), 310
 Bruker, A. B., 270(44), 311
 Bryce-Smith, D., 238(45), 311
 Bub, O., 249(288), 319
 Bubnov, Y. K., 173(16), 197(16), 201(16),
 219
 Bubnov, Yu. N., 261(188), 294(189), 295
 (187, 189), 316
 Bürger, H., 286(46), 285(46), 311
 Bukhtoyarov, I. F., 329(46, 47, 48), 337
 (46, 47, 48), 342(46, 47), 350
 Bulkin, B. J., 245(82b), 307(82b), 312
 Bunsen, R., 170(2), 204(2), 206(2), 219
 Burawoy, A., 196(100), 197(100), 199(100),
 207(100), 222
 Burgemeister, W., 22(198), 24(198), 71
 (198), 88
 Burger, H., 195(99), 222
 Burger, K., 328(9), 349
 Burschkies, K., 2(42), 9(59), 11(42), 49
 (188), 69(59), 71(59), 74(42, 188), 84,
 87
 Bush, J. B., Jr., 236(163), 244(163), 278
 (163), 283(163), 287(163), 315
 Bush, R. P., 8(10), 10(11), 12(11), 13(11),
 27(10), 28(8, 11), 29(8), 30(11), 31
 (9, 11), 33(11), 44(16), 71(10), 75
 (10, 11), 77(11), 83
 Bussen, W., 39(60), 84
 Bussi, I. W., 96(36, 119), 132, 134
- C**
- Cahill, A. E., 341, 349
 Cahours, A., 203(134), 222
 Calabretta, P. J., 12(138), 57(138), 70(138),
 86
 Calas, R., 16(61), 71(61), 84
 Calderazzo, F., 255(47, 48), 256(47, 48),
 257(48a-c), 306(47, 48a-c), 311
 Calingaert, G., 9(62), 23(62), 70(62), 84
 Calloway, N. D., 249(49), 311
 Calvin, G., 335(11), 349
 Camerman, N., 182(54), 185(54), 199(54),
 220
 Cardin, D. J., 284(54), 311
 Carlson, G. L., 180(47), 186(67), 181(47),
 191(47, 67), 220, 221
 Carpenter, C. L., 327(2), 349
 Carraro, G., 253(38), 299(38), 311
 Carter, J. C., 301(265), 318
 Casanova, J., Jr., 253(55, 56), 254(55),
 299(55, 56), 300(55), 311

- Cassol, A., 156(65), 166, 197(109), 222
 Ceron, P., 237(57), 260(57), 311
 Chalk, A. J., 323(34, 35), 324(34, 35), 346(34, 35), 350
 Chalkley, G. R., 245(3), 310
 Challenger, F., 173(19), 174(24), 177(24), 189(83), 197(24), 202(24), 207(155, 158), 210(158, 175), 211(24), 214(158, 175, 185), 215(24), 217(24), 219(19), 220, 221, 223, 224
 Chaltykyan, O. A., 341(12), 349
 Chambers, C., 237(58, 59), 260(58, 59), 311
 Champetier, G., 5(63), 9(63), 21(63), 69(63), 71(63), 72(63), 84
 Chandra, G., 227(61a), 232(61a), 242(61), 248(61), 270(61a), 284(60), 288(60, 61), 289(61), 291(60), 293(61), 311
 Chang, Kuo-King, 269(267), 318
 Chatt, J., 113(2), 125(24), 131, 132, 232(61b), 253(61c), 255(32), 298(61b), 305(32), 310, 311, 324(15), 334(14, 19, 20), 335(16, 17, 18), 338, 349, 350
 Chtyan, G. S., 341(12), 349
 Churchill, M. R., 97(17), 98(17), 101, 102(25, 27, 29, 30), 103(29, 30), 105(28), 107(25, 29, 30), 108(31), 111(28, 31, 34b, 34c), 112(26, 27, 29, 34), 117(11), 125(32, 33), 126(33), 127, 131(27, 34), 131, 132
 Clark, B. F., 260(110), 271(110), 313
 Clark, E. R., 11(64), 71(64), 77(64), 84
 Clark, H. C., 140(16, 18), 146, 153(16), 154(59), 155, 165, 166, 270(12, 62, 63, 64), 275(62), 310, 311
 Clark, R. E. D., 38(65), 84
 Clark, R. L., 204(145), 214(145), 223
 Clauss, A., 114(89), 133
 Clauss, H., 40(131), 41(131), 86
 Clement, W. H., 323(22), 345(21), 350
 Closson, R. D., 230(66), 255(66), 306(65, 66), 307(66), 309(65, 66), 311
 Coates, G. E., 7(49), 8(49), 16(49), 57(49), 84, 139(8), 143(9), 165, 186(64), 197(64), 199(64), 201(64, 120), 202(64), 221, 222, 244(64a), 311, 325(11), 349
 Coffield, T. H., 230(66), 255(66), 306(65, 66), 307(66), 309(65, 66), 311
 Coles, R. F., 204(145, 148), 205(148), 214(145, 148), 223
 Colland-Charan, C., 189(85, 86), 212(85), 221
 Connell, S., 3(140), 8(140), 51(140), 86
 Connolly, J. W., 171(6), 216(6), 219
 Considine, W. J., 23(43), 73(43), 84, 160(82, 83), 161(82, 83), 162(83, 90), 165(90), 167
 Controulis, J., 204(139), 206(139), 214(139), 223
 Cook, A. H., 253(3a), 310
 Cooke, D. J., 54(66), 84
 Cope, F. F., 271(31), 310
 Corey, E. R., 129(35), 132
 Corradine, P., 96(36, 119), 99(37, 38), 132, 134
 Cottis, S. G., 240(100, 101), 266(100, 101), 312
 Cotton, F. A., 94(156), 98, 99, 125, 126, 132, 135, 255(47, 48), 256(47, 48), 306(47, 48), 311
 Cragg, R. H., 234(69, 71), 243(71), 244(71), 247(69, 70), 251(70), 253(70), 281(68, 70, 71), 282(68), 283(69), 286(71), 287(69, 170), 291(68, 69, 70), 297(70), 312
 Cragoe, E. J., 204(145, 148), 205(148), 214(145, 148), 223
 Cramer, R., 323(22a), 326(22a), 350
 Criegee, R., 107(45), 132
 Crosse, B. C., 28(15), 33(15), 36(15), 37(17, 18), 83
 Cullen, W. R., 241(72), 270(72), 271(72, 73), 312
 Cummings, F. E., 235(117), 238(114, 116, 117), 313
 Cummins, R. A., 12(67), 70(67), 84, 165(97), 167, 184(60), 188(60), 213(60), 221
- D**
- Dafert, O. A., 270(74), 312
 Dahl, L. F., 99(9), 101, 102(47), 105(121), 107(54, 120), 111(54, 120), 118(21, 48), 124(76, 137), 125, 128(53), 129(35, 96), 130(7, 8, 9, 23, 49), 131(10, 23, 51), 131, 132, 133, 134
 Dahl, L. P., 96, 131
 Dahling, W., 298(228), 317

- Danek, O., 57(68), 64(68), 70(68), 73(68), 84
- Das-Gupta, H. N., 204(147), 205(149), 223, 271(75, 76, 77), 312
- Davidson, N., 339(49), 342(49) 351
- Davidson, W. E., 3(69), 4(69), 5(69), 8(69, 106), 19(104, 105), 20(104, 105), 22(104, 105), 34(104), 38(104, 105), 53(69, 105), 54(69, 104, 105), 57(69), 58(69), 59(69, 104), 84, 85, 64(69), 69(104, 105), 71(104, 105), 72(69, 104, 105), 73(104), 77(69), 78(69), 80(69), 81(69)
- Davies, A. G., 12(50), 36(70), 56(50), 70(70), 84, 85, 160(77, 85), 161(77, 86, 88), 162(77), 165(86), 167, 232(25, 29, 79b), 233(78), 236(29a), 245(80a), 246(25, 29), 250(25, 79, 80), 278(25, 28), 279(23, 25, 27, 28, 79, 79a), 283(23, 24, 25, 26, 28), 284(28, 29a), 285(23, 25, 28, 29a), 79a, 79b), 288(23, 79a, 79b), 789(24, 27, 79b), 291(24), 292(79b), 296(24, 79, 79b, 80), 298(79b), 310, 312
- Davies, N. R., 323(23, 24), 324(23, 24), 338, 346(23, 24), 350
- Dawson, D. S., 241(72), 270(72), 271(72), 312
- Dawson, J. W., 278(17), 281(17, 18), 282(17, 92), 287(17), 310, 312
- Degener, E., 278(220), 283(220), 291(219), 317
- Degreve, Y., 121(149), 135
- Dehnicke, K., 173(20, 21, 21a), 199(20a), 215(20a), 220, 233(225a), 317
- de Moura Campos, M., 272(50), 273(50, 51, 52, 53), 274(50, 52), 311
- Dersin, H. J., 14(203), 15(203), 21(203), 57(203), 64(203), 73(203), 82(203), 88
- Deusche, H., 99, 132
- Dewar, M. J. S., 8(47), 48(47, 48) 51(47, 48), 59(47), 64(47, 48), 66(47, 48), 84
- Dickens, B., 101, 119(57), 131(56), 132
- Dickopp, H., 295(20), 296(20), 310
- Dietrich, H., 106(59), 109(59), 111(59), 133
- Doak, G. O., 125(91), 133
- Dodge, R. P., 101, 118(64), 133
- Dokunikhin, N. S., 245(80a), 296(80a), 312
- Dolgov, B. N., 211(180), 212(180), 224
- Dollase, W. H., 98(40), 99(40), 132
- Dorokhov, V. A., 253(188a), 298(188a), 316
- Dowell, L. C., 96(22), 132
- Doyle, J. R., 327(2), 349
- Dozono, T., 329(25), 332, 342(25), 343(25), 350
- Drago, R. S., 202(126a), 211(126a), 222
- Drenth, W., 8(32), 66(32), 67(32), 76(32), 78(32), 80(32), 84
- Droll, H. A., 328(66), 350
- Dubovitskii, V. A., 240(273), 274(273), 318
- Duffaut, N., 16(61), 71(61), 84
- Dulova, V. G., 240(275), 241(172, 275), 265(275), 266(277), 267(172, 274, 277), 268(277), 315, 318
- Duncan, W. E., 292(81), 312
- Duncanson, L. A., 335(17), 350
- Dungan, C. H., 30(155a), 42(155a), 87
- Dunitz, J. D., 94(65), 99, 101, 107(67), 133
- Dunn, P., 12(67), 70(67), 84, 184(60), 188(60), 213(60), 221
- Dykstra, F. J., 9(62), 23(62), 70(62), 84

E

- Eaborn, C., 2(71, 73), 9(71, 72), 24(72), 25(72), 35(71, 72), 36(72), 46(73), 69(71, 72), 85, 192(93, 94, 97, 98), 202(93), 203(131), 207(93), 221, 222, 249(33, 34, 82), 293(33, 34, 82), 310, 312
- Ebsworth, E. A. V., 2(74), 40(75), 41(75), 42(76), 45(74), 46(74), 85, 180(50), 183(58), 187(72), 191, 192(50) 194(50, 96), 220, 221
- Edgar, S. A., 73(77), 85
- Edgell, W. F., 245(82b), 307(82a), 312
- Edwards, J. D., 227(82c), 312
- Edwards, J. W., 95, 133
- Effenberger, J., 245(82a), 312
- Ehrlich, R., 197(105b), 199(105b), 202(105b), 222
- Eisch, J. J., 240(84), 261(83), 262(84), 312
- Elpern, B., 204(145, 148), 205(148), 214(145, 148), 223

- Emel'ús, H. J., 9(78, 79, 80), 24(80), 26(78), 27(78), 29(78, 80), 36(80), 37(78), 46(78), 47(78), 69(78, 79, 80), 85, 202(129), 204(138, 141), 211(129), 213(138, 141), 222, 223
- Emel'yanova, O. A., 329(46, 47, 48), 337(46, 47, 48), 342(46, 47, 48), 350
- Emerson, K., 185(62), 221
- Engebretsson, E., 100(69), 133
- Engel, G., 154(60), 166
- Enklaar, C. J., 201(121), 222
- Eskin, Z. T., 8(81), 73(81), 85
- Etienne, A., 204(144), 206(144), 223
- Etienne, Y., 5(63, 82, 83), 6(82, 83), 9(63), 21(63), 69(63), 71(63, 83), 72(63, 82), 74(82, 83), 84, 85
- Evans, J., 253(89a), 312
- Evans, P. R., 204(138), 213(138), 223
- Evers, E. C., 186(65), 196(101, 102), 197(65), 199(65), 201(65), 221, 222
- Forbes, G. S., 187(74), 208(162, 166), 209(162, 166), 211(74), 212(74), 221, 223
- Foss, V. L., 289(89, 177c), 312, 315
- Frankland, E., 253(89a), 312
- Frazer, M. J., 250(90), 294(90), 132
- Freitag, W. O., 186(65), 196(101, 102), 197(65), 199(65), 201(65), 221, 222
- Frey, J., 327(57), 260(57), 311
- Frick, C. E., 272(91), 312
- Friedel, R. A., 116(81, 138), 133, 134, 242(112a), 275(112a), 313
- Friedrich, W., 321(32), 324(32), 329(32), 350
- Friend, N. A. C., 271(245), 272(245), 317
- Fritz, H. P., 99(71), 133
- Fritz, P., 282(92), 312
- Frost, A. A., 332(28), 350
- Fujii, H., 249(93a), 250(93a), 312
- Fujitani, K., 160(76), 164(76), 167
- Funk, H., 271(93), 272(93), 312
- Furukawa, J., 249(93a), 250(93a), 312

F

- Faraglia, G., 143(27, 39), 156(27), 157(27), 165, 166, 211(177), 224
- Farrer, H. N., 143(37), 166
- Fassel, V. A., 187(68), 188(76), 221
- Feeney, J., 237(85), 260(85), 312
- Fegér, F., 23(84), 43(84), 51(84), 85
- Feldl, K., 215(185a), 224
- Fellman, W., 129(96), 133
- Fennessey, J. P., 127, 132
- Fernelius, W. C., 328(26), 350
- Figgis, B. N., 126, 133, 161(88), 167
- Filbey, A. H., 306(160), 314
- Finch, A., 237(57), 260(57), 311
- Fink, W., 236(87), 278(86, 87), 279(87), 283(87), 284(86), 312
- Fischer, E. O., 99, 107(72), 133, 135, 201(123), 222, 306(88), 312
- Fischer, H., 35(27), 39(60), 84
- Fischer, B. E., 246(143, 144), 314
- Fisher, E. D., 337(27), 350
- Flagg, E. E., 337(73), 351
- Flath, R. A., 5(154), 21(154), 72(154), 86
- Flato, J., 271(243, 244), 272(243), 317
- Fliegel, P., 321(32), 324(32), 329(32), 350

G

- Gaeva, L. A., 245(80a), 296(80a), 312
- Gaidis, J. M., 220
- Gar, T. K., 240(93b, 191, 192, 193), 267(93b), 268(93b, 191, 192, 193), 312, 316
- Garland, J. H. N., 251(1, 2), 297(1, 2), 310
- Garner, C. S., 328(75), 351
- Gavlin, G., 312
- Gavrilenko, V. V., 248(290), 319
- Gavrilov, G. I., 73(259), 89
- Gavron, J. L., 173(18), 204(18), 205(18), 206(18), 219(18), 220
- Gayoso, M., 173(21), 220, 233(225a), 317
- Gellman, M. I., 328(30), 350
- Gent, W. L., 197(110), 199(110), 214(10), 222
- George, T. A., 13(85), 41(85), 54(85), 85, 233(95), 234(95), 237(96), 241(95, 96), 247(95), 248(95), 251(96), 253(95, 96), 261(96), 265(96), 268(96), 269(96), 270(96), 283(95), 287(95), 289(95), 291(95), 292(95), 293(95), 297(96), 298(95), 301(96), 312

- Gerloch, M., 96(74), 97(17), 98(17), 101(12), 102(73), 112(12), 131(12), 131, 133
- Gerrard, W., 143(29), 157(29), 166, 227(81b), 249(96a), 250(90), 253(96a), 294(90), 312
- Gibbons, A. J., Jr., 160(74, 83), 161(83), 162(83), 167
- Gibson, C. S., 196(100), 197(100, 110), 199(100, 110), 207(100), 214(110), 222, 271(11), 272(13), 310
- Gibson, D. T., 22(86), 85
- Gibson, G. K. J., 298(97), 312
- Gilland, R. D., 113(75), 133
- Gillespie, R. J., 40(87), 85, 145(42, 43, 44), 166
- Gilman, H., 2(109, 142), 8(90), 16(256), 17(91, 255), 19(89), 22(109), 24(90), 25(90, 91, 255), 34(89, 91, 255), 52(89, 90, 255, 256), 57(88), 71(89, 256), 85, 86, 89, 138(1), 141(1), 159(1, 71), 165, 167, 173(15), 200(15), 203(135, 137), 204(137), 207(157), 208(15), 209(135), 210(137), 211(15), 213(135, 137), 214(157), 219(137), 219, 222, 223, 224, 237(101a, 106, 108a), 240(98, 99, 100, 101), 244(109, 109a), 248(104, 105, 108), 249(104, 106), 251(102, 103, 105, 107), 253(106a, 109b), 264(99), 265(98), 266(100, 101), 312, 313
- Gilson, T., 138, 149(3), 165
- Gingold, K., 8(92), 73(92), 85
- Ginsberg, A. P., 96(1), 131
- Ginsburg, V. A., 73(259), 89
- Gipstein, E., 260(110), 271(110), 313
- Gitlitz, M. A., 248(35), 292(35), 310
- Giustiniani, M., 143(27), 156(27), 157(27), 165, 211(177), 224
- Gleiter, R., 245(82a), 312
- Glick, M. D., 124(76), 133
- Glovaki, G. R., 212(182), 224
- Goddard, A. E., 211(179), 224
- Godin, G. W., 323(29), 350
- Gohlke, R. S., 263(152, 153), 267(152, 153), 268(152, 153), 314
- Gol'danskii, V. I., 165, 167
- Goldfarb, T. D., 40(93), 85
- Goldstein, E. J., 240(260), 264(260), 318
- Goldsworth, L. J., 204(143), 205(143), 206(143), 223
- Goller, H., 16(46), 18(46), 19(46), 22(46), 34(46), 52(46), 69(46), 71(46), 84
- Gonsior, L. J., 261(83), 312
- Goubeau, J., 40(94, 95), 85, 178(38, 40, 41), 179(38, 41), 186(38, 40), 187(38), 188(41), 199(38, 115), 208(38), 220, 222
- Gräbner, H., 178(38), 179(38), 186(38), 187(38), 199(38), 208(38), 220
- Graham, I. F., 160(85), 167
- Grdenic, D., 291(111a), 313
- Green, L. D., 249(49), 311
- Green, M., 242(8, 10), 275(8, 10), 306(9, 111b), 257(111b), 313, 397(9), 310
- Green, M. L. H., 96(77, 79), 105(78), 107(90), 133, 233(111c), 313
- Green, S. J., 270(112), 313
- Greenfield, H., 116(81, 138), 133, 134, 242(112a), 275(112a), 313
- Greenwood, N. N., 178(43, 45), 189(43, 45), 218(43), 219(45), 220
- Greer, W. N., 139(5), 165
- Griffith, W. P., 275(112b), 313
- Griffiths, J. E., 191(88), 221
- Grim, S. O., 156(63), 166
- Grimber, A. A., 328(30), 350
- Grimm, A., 61(183), 87
- Groizeleau, L., 249(113), 313
- Grüttmer, G., 6(96), 8(97, 98, 99), 51(99), 70(97), 73(96, 98, 99), 85
- Grumer, E., 39(60), 84
- Gulden, W., 253(134), 314
- Guy, R. G., 113(2), 131, 324(31), 326(31), 350

H

- Haag, R., 254(130), 261(130), 314
- Haas, A., 24(100), 85
- Hafner, W., 321(32, 66, 67), 323(66, 67), 324(32, 66, 67), 325(66), 326(66), 329(32, 66, 67), 330(67), 331(67), 332(67), 336(67), 342(67), 344(66), 345(67), 350, 351
- Haiduc, I., 2(29), 6(30), 84
- Haiss, H. S., 142(25), 143(25), 165
- Halevy, J., 173(19), 220

- Halpern, J., 233(113a), 313, 334(33), 350
 Hamilton, C. S., 204(145, 148), 205(148), 214(145, 148), 223, 271(7), 310
 Hamilton, W. C., 130(107), 134
 Hampson, H., 49(48), 51(48), 64(48), 84
 Hancock, M., 160(77), 161(77, 86), 162(77), 165(86), 167
 Hantzsch, A., 206(154), 214(154), 223
 Harada, T., 9(101), 70(101), 73(101), 85
 Hardgrove, G. L., 94(82), 133
 Harman, A. B., 235(117), 238(115, 116, 117), 313
 Harman, K. M., 235(117), 238(114, 115, 116, 117), 313
 Harrod, J. F., 323(34, 35), 324(34, 35), 346(34, 35), 350
 Hartman, F. A., 293(117a), 313
 Hashimoto, T., 249(33, 34, 82), 293(33, 34, 82), 310, 312
 Haszeldine, R. N., 204(141), 213(141), 223, 242(8, 10), 275(8, 10), 306(9), 307(9), 310
 Hathaway, B. J., 140(15, 17), 153(15), 165
 Hatlelid, E. B., 204(145), 214(145), 223
 Hatton, J. V., 202(126), 211(126), 222
 Haubein, A. H., 237(101a), 312
 Hawthorne, M. F., 129(83, 84, 85), 133, 295(118, 119), 313
 Hayashi, M., 40(169), 87
 Heandler, H. M., 156(64), 166
 Heap, R., 10(102), 10(103), 14(103), 23(102), 26(102), 57(102, 103), 64(103), 85
 Heck, R. F., 232(125a), 233(125a), 234(125a), 242(123, 124), 125a, 254(125a), 255(119a, 127, 127a, 128, 129), 275(123, 124), 307(119a, 120, 121, 126, 127, 127a, 128, 129), 308(120, 125, 129), 309(121a, 122), 313, 314
 Hedberg, K., 39(20), 40(20), 83
 Heffer, J. P., 348(58), 357
 Hendifar, A., 172(10), 202(10), 207(10), 209(10), 212(10), 219
 Henry, M. C., 3(69), 4(69), 5(69), 8(69), 10(106), 14(106), 15(127), 19(104, 105), 20(104, 105, 106), 22(104, 105), 26(106), 29(106), 34(104), 38(104, 105), 53(69, 105), 54(69, 104, 105), 57(69, 106), 58(69, 106), 59(69, 104), 64(69), 69(104, 105), 70(127), 71(104, 105), 72(69, 104, 105), 73(104, 127), 77(69), 78(69), 80(69), 81(69), 84, 85, 86
 Henry, P. M., 325(37), 329(36, 37), 330(36), 332, 333, 335, 336, 337, 342, 350
 Herberich, G. E., 107(72), 133
 Hesse, G., 253(131, 132, 133, 134), 254(130), 261(130), 299(131, 132), 300(132, 133), 301(133), 314
 Heubach, E., 178(40), 186(40), 199(115), 220, 222
 Hewett, C. L., 270(135, 136), 314
 Heying, T. L., 280(137), 281(137), 287(137), 314
 Hibbert, H., 206(154), 214(154), 223
 Hiersemann, W. D., 40(95), 85
 Higgins, M. A., 260(110), 271(110), 313
 Hill, J. A., 251(1, 2), 297(1, 2), 310
 Hillman, M. E. D., 255(138, 139, 140), 302(138, 139), 303(138, 139, 140), 304(138, 140), 305(138, 139), 314
 Hilla, K., 3(69), 4(69), 5(69), 8(69), 53(69), 54(69), 57(69), 58(69), 59(69), 72(69), 84
 Hinkel, L. E., 201(120), 222
 Hinz, G., 294(186a), 306(186a), 316
 Hirschmann, R. P., 187(68), 188(76), 221
 Hock, A. A., 120(86, 87), 133
 Hodgkin, D. C., 127, 134
 Hölzle, G., 273(141), 314
 Hofferth, B., 173(15), 200(15), 208(15), 211(15), 219
 Hoffmann, H., 8(132), 9(132), 23(132), 26(132), 41(132), 46(133), 70(132), 73(132), 74(132), 82(132), 86, 151(55), 166
 Holliday, A. K., 237(58, 59, 85), 260(58, 59, 85), 311, 312
 Holt, S., 196(100), 197(100), 199(100), 207(100), 222
 Holtschmidt, H., 278(220), 283(220), 284(218), 287(218, 220), 291(216, 217, 218, 219), 292(217), 317
 Holzapfel, H., 197(105a), 222
 Hoogzand, C., 109(106), 114(89), 133, 134
 Hook, W. H., 204(143), 205(143), 206(143), 223

- Hooton, K. A., 3(107), 9(107), 19(107), 23(107), 24(107), 25(107), 29(107), 34(107), 35(107), 41(107), 42(107), 51(107), 52(107), 53(107), 54(107), 59(107), 64(107), 65(107), 66(107), 67(107), 81(107), 85
- Hopkins, T. E., 129(159), 135
- Hoppe, W., 99, 132
- Horder, J. R., 244(142), 245(142), 247(142), 282(142), 287(142), 289(142), 290(142), 314
- Horwitz, J. P., 246(143, 144), 314
- Hota, N. K., 271(73), 312
- Howarth, O. W., 189(82), 213(82), 221
- Hoyer, H., 187(71), 221
- Hübel, W., 109(106), 114(89), 117(88), 122(153), 130(23), 131(23), 132, 133, 134, 135
- Huber, F., 9(108), 12(108), 15(108), 70(108), 85
- Hughes, D. W., 298(97), 312
- Huisgen, R., 227(144a), 314
- Hulme, R., 139(8), 154(8), 165
- Huls, R., 189(85), 212(85), 221
- Hunt, A. J., 271(145), 314
- Hunt, R., 117(11), 131
- Hurd, D. T., 175(31), 220
- Hurenkamp, J. B. G., 9(33), 39(33), 81(33), 82(33), 84
- Hyatt, D. E., 300(146), 314
- Jahnke, D., 244(238, 239), 247(238a), 253(238), 279(239), 280(239), 282(239), 287(239), 291(238a), 295(238a), 317
- Jakovlev, I. P., 253(188a), 298(188a), 316
- Jakusik, E. R., 16(135), 64(135), 73(135), 86
- Janssen, M. J., 16(160), 17(159), 55(160), 87, 140(13, 14, 21), 149(50), 165, 166, 199(113, 114), 217(113), 222
- Janzen, A. J., 296(147a), 314
- Jasching, W., 50(110), 85
- Jefferson, R., 234(149), 236(149), 243(149), 280(148), 281(148), 288(149), 289(149), 314
- Jellinek, F., 95(92), 98, 99, 133
- Jenkins, C. R., 44(16), 83
- Jenkins, D. R., 187(72a, 73), 191, 221
- Jenne, H., 278(17), 281(17), 282(17), 287(17), 310
- Jennings, J. R., 253(150a), 298(150), 314
- Jenny, W., 273(141, 151), 314
- Jira, R., 321(32, 66, 67), 323(66, 67), 324(32, 66, 67), 325(66), 326(66), 329(32, 66, 67), 330(67), 331(67), 332(67), 336(67), 342(67), 344(66), 345(67), 350, 351
- Job, A., 201(119a), 222
- Jörg, H., 3(114), 86
- John, J. A., 204(143), 205(143), 206(143), 223
- Johnson, F., 263(152, 153), 267(152, 153), 268(152, 153), 314
- Johnson, O. H., 2(111), 85
- Johnson, W. A., 50(112), 86
- Jones, D. J., 233(111b), 313
- Jones, K., 13(85), 41(85), 54(85, 113), 85, 86, 233(95), 234(95, 155b), 235(155b), 243(154), 247(95), 248(95), 251(155a, 155b), 252(155a, 155b), 253(95, 155, 155a, 155b), 283(95, 154), 287(95, 155), 289(95, 155), 291(95, 154), 292(95), 293(95), 298(95, 155), 312, 314
- Jones, N. D., 95(95), 133
- Jones, R. G., 248(104, 105), 249(104), 251(102, 103, 105), 313
- Jones, W. E., 270(136, 156), 314
- Joy, F., 235(158), 237(158), 238(157, 158), 239(158), 240(158), 259(157, 158), 260(157), 261(157, 158), 314

I

- Ibers, J. A., 99, 130(107), 133, 134
- Immirzi, A., 99(6), 100(6), 101(123), 131, 134
- Inatome, I., 251(147), 297(147), 314
- Ingham, R. K., 2(109), 22(109), 85, 138, 141(1), 159(1, 71), 165, 167, 203(135), 209(135), 213(135), 222
- Ishida, S., 286(221), 317
- Ito, M., 329(76), 333(76), 351
- Ivanova, I. L., 289(177c), 315
- Ivanova, M. A., 328(64, 65), 351

J

- Jacobi, K. R., 201(122), 222
- Jaffé, H. H., 125(91), 133

Joy, V. J. R., 329, 350
 Jungfleisch, E., 225, 271(14, 15, 16), 310
 Jutzi, P., 241(259), 284(258), 288(258),
 291(258), 318

K

Kabe, H. J., 263(159), 314
 Kaesz, H. D., 129(96), 133
 Kahlen, N., 174(30), 182, 195(30, 56),
 196(30, 56), 203(30), 212(30), 213(30),
 220
 Kahler, F. H., 204(145), 214(145), 223,
 271(7), 310
 Kaluski, Z. L., 95(97, 98, 99), 133, 134
 Kasai, N., 147(46), 150(52), 151(57), 153
 (57), 164(92), 166, 167
 Kaska, W., 240(84), 262(184), 312
 Katada, K., 186(66), 187(66), 191(66),
 192(66), 221
 Kawakami, K., 140(40), 156(66), 157(40),
 158(66), 166, 167, 188(81), 213(81),
 221
 Kawasaki, Y., 143(28, 31, 38, 41), 147(46),
 155(28), 157(28), 158(31), 165, 166
 Keane, F. M., 217(195, 196), 224
 Keblys, K. A., 306(160), 314
 Keeber, W. H., 13(115), 51(115), 86
 Keeton, M., 113(75), 133
 Keith, J. N., 196(101), 222
 Keller, P. C., 173(23), 174(23), 215(23),
 220
 Kellermann, K., 170(1), 219
 Kent, R. A., 263(265b), 318
 Kenyon, A. S., 50(116), 86
 Kerrigan, J., 237(57), 260(57), 311, 318
 Kettle, S. F. A., 104(102), 110, 130(100,
 101), 134
 Kewley, R., 187(72a, 73), 191(73), 221
 Khachaturov, A. S., 240(199), 268(199),
 316
 Khananaishvili, L. M., 2(29), 6(30), 84
 Kharasch, M. S., 232(160a), 248(160a),
 251(160a), 252(160a), 315, 324, 326,
 344, 350
 Khotyanova, T. L., 95(143, 144), 135,
 271(262), 318
 Khrapov, V. V., 165(94), 167

Kiefer, H. R., 253(55), 254(55), 299(55),
 300(55), 311
 Kikuchi, S., 329(76), 333(76), 351
 Kimura, K., 186(66), 187(66), 191, 192(66),
 221
 King, G. S. D., 114(89), 122(122), 123
 (104), 131(104), 133, 134
 King, R. B., 126, 134
 Kington, G. L., 95(68), 133
 Kippur, P. R., 260(110), 271(110), 313
 Kirby, R. H., 237(106), 249(106), 253
 (106a), 313
 Kiseleva, N. V., 328(30), 250
 Kiselev, V. G., 294(189), 295(189), 316
 Kitching, W., 232(161), 240(161), 315
 Kjaer, A., 180(49), 220
 Klasens, H. A., 8(34), 39(34, 117, 118, 119),
 66(34), 67(34), 84, 86
 Klason, M. P., 67(120), 86
 Klebe, J. F., 236(163), 244(163), 252(162a),
 278(163), 283(163), 286(162), 287
 (163), 315
 Kleinberg, J., 337(41), 350
 Klippel, J., 2(121), 70(121), 86
 Klug, H. P., 116(145), 124(145), 131(145),
 135
 Kniseley, R. N., 187(68), 188(76), 221
 Knoth, W. H., 174(29), 183(29), 194(29),
 202(29), 207(29), 208(29), 220
 Knox, G. R., 292(22), 310
 Knox, K., 96(1), 131
 Kochi, J. K., 348(42), 350
 Köster, R., 140(19), 165, 232(164a), 233
 (164a), 239(164, 164a), 240(164a),
 260(164), 315
 Koizumi, N., 245(82b), 307(82b), 312
 Kojer, H., 321(66), 323(66), 324(66), 325
 (66), 326(66), 329(66), 344(66), 351
 Kolbezan, M. J., 224
 Kolesnikov, S. P., 240(198, 199), 268
 (198, 199, 200), 316
 Komura, M., 143(28), 155(28), 157(28),
 165
 Kondo, M., 43(139), 86
 Kononova, M. A., 328(64, 65), 351
 Koresnikov, Yu. D., 240(275), 241(275,
 275a), 265(275), 318
 Koten, I. A., 248(164b), 292(164)b, 315
 Koton, M. M., 14(178), 87

Kozeschkow, K. A., 8(81, 125, 170), 15
(125), 70(157), 72(122, 124, 125, 170,
231), 73(81), 74(123, 125), 85, 86,
87, 89
Kozik, B. L., 323(43), 324(43), 350
Kozikowski, J., 230(66), 255(66), 306
(65, 66), 307(66), 309(65, 66), 311
Kramer, J., 8(35, 36), 23(36), 36(36), 64
(36), 67(35), 68(35, 36), 80(36), 84
Kratzer, R. H., 194(91), 195, 221
Kraus, C. A., 15(126), 23(126), 26(126),
70(126), 86, 139(5), 165
Krause, E., 8(98, 99), 51(99), 73(98, 99),
85, 172(12), 201(125), 204(140), 206
(140), 207(159), 211(125), 215(12),
219, 222, 223
Krebs, A. W., 8(106), 10(106), 14(106),
15(127), 20(106), 26(106), 29(106),
57(106), 58(106), 70(127), 73(127),
85, 86
Krekeler, H., 322(68), 323(68), 324(68),
351
Kretschmar, G., 244(239), 279(239), 280
(239), 282(239), 287(239), 317
Kriegsmann, H., 8(132), 9(132), 23(132),
26(132), 40(128, 129, 130), 41(130,
131, 132), 46(133), 70(132), 73(132),
74(132), 82(132), 86, 148(47), 151(55),
166
Kriner, W. A., 186(65), 196(101, 102),
197(65), 199(65), 201(65), 221, 222
Kroll, W. R., 262(164), 315
Kruerke, U., 109(106), 114(89), 133, 134
Kruger, C., 14(238), 89
Krupp, F., 248(293), 249(293), 293(293),
319
Kuchen, W., 9(79), 69(79), 85, 202(129,
130), 211(129, 130), 222
Kuckertz, H., 14(238), 89
Kuhn, L. P., 251(147), 297(147), 314
Kuivila, H. G., 15(134), 16(135), 64(135),
72(134), 73(135), 86
Kullmann, R., 5(63), 9(63), 21(63), 69(63),
71(63), 72(63), 84
Kulmiz, P., 2(136, 137), 11(137), 70(136,
137), 86
Kupchik, E. J., 12(138), 57(138), 70(138),
86
Kuran, W., 233(228a), 298(229), 317

Kurita, Y., 43(139), 86
Kursanov, D. N., 240(273, 275), 241
(275, 275a), 263(276), 265(275), 266
(276, 277), 267(274, 276, 277), 268
(277), 274(273), 318
Kurwada, D., 253(55), 254(55), 299(55),
300(55), 311
Kuzashev, M. V., 295(266), 318

L

Lake, K. J., 46(241), 89
La Mer, V. K., 333(63), 351
Langer, S. H., 3(140), 8(140), 51(140), 86
La Placa, S. J., 130(107), 134
Lappert, M. F., 13(85), 41(85), 54(85, 113),
85, 86, 170(4), 178(39), 187(39, 70),
188(39), 198(39), 199(39), 208(4, 39,
161), 211(4, 39), 219, 220, 221, 223,
227(61a, 82c), 232(61a), 233(95),
234(69, 71, 95, 149, 155b, 158, 167,
168), 235(155b), 236(149), 237(96,
158, 166a, 168), 238(157, 158, 166,
166a), 239(158, 166a), 240(158), 241
(95, 96), 242(61), 243(71, 149, 154,
167), 244(71, 142), 245(142, 169a),
247(69, 70, 95, 142, 169, 170), 248(61),
249(96a), 250(90), 251(70, 96, 155a,
155b, 169, 170), 252(155a, 155b), 253
(70, 95, 96, 96a, 155, 156a, 155b, 169,
170), 259(157, 158, 166), 260(157),
261(96, 157, 158, 168), 265(96), 268
(96), 269(96), 270(61a, 96), 278(169),
280(148, 167), 281(68, 70, 71, 148,
170), 282(68, 142), 283(69, 95, 154),
284(54, 60), 285(167), 286(71), 287
(69, 95, 142, 155, 167, 170), 288
(60, 61, 149), 289(61, 95, 142, 149, 155,
169, 170), 290(142), 291(60, 68, 69,
70, 95, 154, 170), 292(95), 293(61, 95),
294(90), 297(70, 96, 170), 298(95, 155),
301(96), 311, 312, 314, 315
Larbig, W., 248(293), 249(293), 293(293),
319
Larkworthy, L. F., 251(1, 2), 297(1, 2), 310
Larsson, E., 13(141), 21(141), 69(141),
71(141), 86
Latimer, W. M., 328(44), 339(44), 350

- Lawhead, J., 204(145), 214(145), 223
 Lee, T. Y., 96(158), 135
 Leeper, R. W., 2(142), 86, 203(137), 204(137), 210(137), 213(137), 219(137), 222
 Leffler, J. E., 171(5), 215(5), 219
 Lehmkuhl, H., 240(171), 262(171), 291(171), 315
 Lehnardt, R., 8(168), 73(168), 87
 Leites, L. A., 241(172), 267(172), 315
 Lenhert, P. G., 127, 134
 Lesbire, M., 17(143), 52(143), 86, 283(246), 287(246), 291(246), 317
 Lewis, J., 126(70), 133, 180(78), 188(78), 221
 Lewis, R. N., 175(31), 220
 Lewis, W. L., 270(173, 174), 315
 Li, Shih-Tsin, 204(142), 223
 Lichtenwalter, G., 19(89), 34(89), 52(89), 73(89), 85
 Lichtenwalter, M., 253(106a), 313
 Lieber, E., 188(75), 217(195, 196), 221, 224, 246(175), 315
 Lile, W., 8(144), 11(144), 73(144), 86
 Limburg, W. W., 289(172), 315
 Lindsey, R. U., 174(29), 183(29), 194(29), 202(29), 207(29), 208(29), 220
 Linnett, J. W., 190(87), 221
 Linton, R. H., 40(145), 86, 182, 220
 Lionetti, A., 101(123), 134
 Lipscomb, W. N., 101, 119(57), 131(56), 132
 Lloyd, J. E., 298(150, 177), 314, 315
 Lobanera, O. A., 328(64, 65), 351
 Lockhart, J. C., 211(178), 224
 Lohmann, D. H., 165(98), 167
 Long, R. F., 126(70), 133
 Loosen, K., 39(263), 89
 Lorberth, J., 140(20), 165, 199(111), 203(111), 222
 Lorenz, D. H., 17(146), 70(146), 86
 Ludwig, P., 107(45), 132
 Lübke, K., 203(136), 222
 Luijten, J. G. A., 2(148, 149), 70(149), 78(147), 86, 140(13, 14, 21), 149(50), 165, 166, 199(113, 114), 200(119), 217(113, 119), 222
 Lukevits, E. Y., 232(177a), 233(177a), 315
 Lupin, M. S., 275(177b), 276(177b), 315
 Lutsenko, I. F., 241(179), 270(179), 289(89, 177c, 178, 232), 296(233), 312, 315, 317
 Lydon, J. E., 108(108), 134
 Lynch, J., 227(61a), 232(61a), 270(61a), 311
 Lynds, L., 259(261), 260(261), 318
 Lyons, J. E., 236(163), 244(163), 278(163), 283(163), 287(163), 315
- ### M
- Maasböl, A., 306(88), 312
 McBride, J. J., 181(51), 182, 183(51), 200(51, 116), 202(128), 207(128), 211(128), 220, 222
 McCleverty, J. A., 96(77), 126, 132, 133, 315
 McCombie, H., 10(150), 12(150), 57(150), 86, 207(156), 223
 McConnell, H., 339(49), 342(49), 351
 MacDiarmid, A. G., 2(151, 153), 43(152), 46(227), 86, 88, 174(27), 186(65), 196(101, 102), 197(65), 199(65), 201(65), 202(27), 203(27), 207(27), 209(168), 220, 221, 222, 223, 291(245b), 317
 McDonald, A. C., 95(109), 134
 McGrady, M. M., 143(30, 32, 37), 144(30), 145(30), 157(30), 158(30, 32), 166
 McIntyre, P., 271(244), 317
 McKenzie, A., 206(152), 223
 McNinth, H. A., 17(255), 25(255), 34(255), 52(255), 89
 McQuillan, G. P., 139, 142(7), 144(7), 154, 155(7), 165
 Magin, A., 302(241), 303(241), 305(241), 317
 Maguire, R. G., 312
 Majert, H., 294(186a), 306(186a), 316
 Makarov, E. F., 165(94), 167
 Makarov, S. P., 73(259), 89
 Makarova, L. G., 232(179a), 315
 Malz, H., 278(220), 283(220), 284(218), 287(218, 220), 291(216, 217, 218, 219), 292(217), 317
 Manakov, M. N., 240(201, 202, 203, 204, 205, 206), 264(201, 202, 203, 205, 206), 265(206), 266(201), 268(204), 316
 Manchot, J., 99(71), 133

- Mann, F. G., 270(180), 315
 Manuel, G., 267(182, 185a), 315
 Manuel, T. A., 233(181), 279(181), 285
 (181), 315
 Margrave, J. L., 263(265b), 318
 Maričić, S., 112(110), 134, 326(45), 350
 Marin, R., 13(141), 21(141), 69(141), 71
 (141), 86
 Markby, R., 116(81, 138), 133, 134, 242
 (112a), 275(112a), 313
 Marple, K. E., 248(108), 251(107), 313
 Marsden, F. J., 237(85), 260(85), 312
 Marsh, R. E., 95(95, 151), 130(20), 132,
 133, 135
 Martel, B., 16(61), 71(61), 84
 Martin, D., 187(69), 221
 Martin, D. F., 143(33, 35), 157(33), 158
 (67), 166, 167
 Masada, H., 307(263), 318
 Mason, R., 95(68), 96(74), 97(16, 17), 98
 (17, 18), 101(12), 102(25, 27, 29, 73),
 103(29), 104(102), 105(28), 107(25,
 29), 109(112), 110, 111(28, 112), 112
 (12, 13, 26, 27, 29, 34), 113(75), 117
 (11, 13), 125(111), 126(70, 111), 130
 (18, 19), 131(12, 13, 27, 34), 131, 132,
 133, 134
 Mastryukov, V. S., 266(277), 267(277),
 268(277), 318,
 Matsiashek, S. A., 253(229a), 317
 Matsumoto, A., 150(52), 166
 Matveev, K. I., 329(46, 47, 48), 337(46,
 47, 48), 342(46, 47, 48), 350
 Mawby, R. J., 255(183, 184), 256(183),
 257(184), 306(183, 184, 185), 315
 Mayfield, D. L., 5(154), 21(154), 72(154),
 86
 Mayo, F. R., 324(40), 326(40), 344(40), 350
 Mays, M. J., 180(50), 191, 192(50), 194
 (50, 96), 220, 221
 Mazerolles, P., 267(182, 185a), 315
 Meals, R. N., 237(108a), 313
 Meerwein, H., 294(186a), 306(186a), 316
 Melvin, H. W., 173(15), 200(15), 208(15),
 211(15), 219
 Menzies, R. C., 8(144), 11(144), 73(144),
 86
 Merenyi, R., 122(153), 135
 Merkulova, E. N., 73(259), 89
 Meunier-Piret, J., 121(149), 122(113, 122),
 125(113), 126(113), 134, 135
 Mez, H. C., 101(67), 107(67), 133
 Michaud, H., 173(17), 215(17), 220
 Mieg, W., 213(184a), 224
 Mikhailov, B. M., 173(16), 197(16), 201
 (16), 219, 253(188a), 257(190), 261
 (188), 294(189), 295(187, 189), 298
 (188a), 316
 Miller, C. J., 22(86), 85
 Miller, F. A., 186(67), 188(77), 191(67),
 221
 Mills, O. S., 99(15), 101(67), 107(67),
 109(117), 120(86, 87, 118), 124(114,
 117), 131, 133, 134, 277(265a),
 318
 Miltag, E., 5(236), 89
 Mironov, V. F., 240(93b, 191, 192, 193),
 267(93b), 268(93b, 191, 192, 193), 312,
 316
 Mitsutani, A., 329(50), 342(50), 351
 Moedritzer, K., 30(155, 155a), 42(155a),
 73(155), 81(155), 87
 Moiseev, I. I., 323(54), 324(51, 53, 54, 80),
 325(56), 326(54), 329(78, 79, 81),
 330(55), 333(81), 334(54, 57, 81),
 336(54, 55, 56, 57, 79, 81), 337(56),
 344(53, 54), 345(4), 346, 347, 348(53),
 349(5), 349, 351, 352
 Mole, T., 249(194, 195), 250(194), 316
 Mooney, E. F., 143(29), 157(29), 166
 Morehouse, S. M., 348(58), 351
 Morgan, G. T., 206(153), 223
 Morgan, J. F., 204(145, 148), 205(148),
 214(145, 148), 223
 Morgunova, M. M., 283(292), 319
 Morris, D., 306(185), 315
 Mould, R., 187(72), 221
 Muecke, A., 61(156, 183), 87
 Müller, H., 8(199), 21(199), 23(199, 200),
 59(199), 64(109), 66(199), 72(199),
 80(199), 88, 239(285), 262(285), 319
 Muetterties, E. L., 159(69), 167, 250(197),
 294(197), 316
 Mufti, A. S., 142(26), 160(80), 161(80),
 165, 167, 174(28), 187(28), 197(28),
 209(28), 210(28), 220
 Mukherjee, R. N., 186(64), 197(64), 199
 (64), 201(64), 202(64), 221

N

- Nad, M. M., 70(157), 73(124), 74(123), 86, 87
 Nagel, K., 262(294), 319
 Nagy, P. L. I., 133
 Nakamura, Y., 160(81), 167
 Nambury, C. N. N., 246(175), 315
 Nametkin, N. S., 5(158), 43(234), 69 (158, 234), 71(158, 234), 87, 89
 Napoli, M. J., 240(280), 264(280), 319
 Nasutavicus, W. A., 263(153), 267(153), 268(153), 314
 Natta, G., 96(119), 137
 Nefedor, O. M., 240(198, 199, 201, 202, 203, 204, 205, 206), 264(201, 202, 203, 205, 206), 265(206), 266(201), 268 (198, 199, 200, 204), 316
 Nehmé, M., 292(207), 316
 Nekheeva, N., 84
 Nekrassov, A. S., 270(208), 314
 Nekrassov, W. W., 270(208), 316
 Nelson, J. F., 244(109), 313
 Nelson, W. H., 143(33, 35), 157(33), 166
 Nenning, P., 197(105a), 222
 Neruda, B., 216(190), 224
 Nesmeyanov, A. N., 8(81, 125), 15(125), 73(81, 125), 74(125), 85, 86, 232(179a), 262(211), 271(209, 210), 315, 316
 Neumann, W. P., 140(19), 165
 Nicholson, J. K., 108(108), 134
 Nickless, G., 44(173), 54(66), 84, 87
 Niedenzu, K., 278(17), 281(17, 18), 282 (17, 92), 287(17), 310, 312
 Nikolaeva, M. E., 287(190), 316
 Nishino, M., 160(78), 161(78), 163(78), 167, 188(80), 197(80), 213(80), 221
 Nixon, E. R., 40(145), 86, 182, 220
 Noack, K., 257(48a-c), 311
 Nöth, H., 237(269), 248(215), 279(269), 292(269), 270, 271, 316, 318
 Nogina, O. V., 240(273), 274(273), 318
 Noltes, J. G., 2(161), 16(160), 17(159, 162), 55(160), 70(161, 162), 87, 278(213), 284(212), 285(213), 287(213), 288 (212, 213, 214), 316
 Nomura, T., 5(163), 21(163), 39(261), 72(163), 87, 89

- Nord, H., 341(59), 351
 Norris, J., 204(146), 223
 Nyholm, R. S., 126(70), 133, 145(42), 166, 180(78), 188(78), 221, 233(215a), 316

O

- Oberhansli, W. E., 105(121), 107 (54, 120), 111(54, 120), 132, 134
 O'Brian, T. A., 111(34b), 132
 O'Brien, R. J., 140(16, 18), 146(45), 153 (16, 59), 154(59), 155, 165, 166
 O'Donnell, G., 237(101a, 108a), 312, 313
 Odyakov, V. F., 329(46, 47), 337(46, 47), 342(46, 47), 350
 Oertel, G., 278(220, 237), 280(237), 282 (237), 283(220), 284(218), 287(218, 220, 237), 219(216, 217, 218, 219), 292(217), 317
 Oga, T., 329(76), 333(76), 351
 Ohara, M., 149(51), 160(81), 166, 167
 Okawara, R., 41(57), 46(164), 73(57), 84, 87, 138, 140(15, 24), 143(28, 31, 34, 38, 40, 41), 146(2), 148(49), 149(51), 150(2, 34, 52), 151(53, 56, 57), 153 (15, 57, 58), 154(24, 58), 155(28, 61), 156(24, 66), 157(28, 40), 158(31, 66), 160(72, 73, 75, 76, 78, 81, 84), 161 (4, 75, 78, 84), 162(75), 163(24, 56, 75, 78), 164(76, 91, 92), 165, 166, 167, 188(80, 81), 192(89), 197(80), 198, 213(80, 81), 221
 Okuda, Y., 307(263, 264), 318
 Olson, D. H., 139(12), 165
 Onak, T. P., 233(220a), 317
 Onyszychuk, M., 9(78, 79), 26(78), 27(78), 29(78), 37(78), 46(78), 47(78), 69 (78, 79), 85, 202(129), 211(129), 222
 Orchin, M., 233, 317, 329, 350
 Orgel, L. E., 94(65), 133
 Osipov, A. M., 329(46, 47), 337(46, 47), 342(46, 47), 350
 Ott, E., 292(81), 312
 Ourston, P. G., 127, 134
 Ovarov, L. S. P., 43(234), 69(234), 71(234), 89
 Overberger, C. G., 286(221), 317
 Owen, D. A., 301(146), 314

P

- Pacault, A., 44(166), 67(166), 87
 Paciorek, K. L., 194(91), 195(91), 221
 Padberg, F. J., 9(108), 12(108), 15(108), 70(108), 85
 Paetzold, P. I., 173(21), 197(106), 215(186), 220, 222, 224, 233(222, 223, 224, 225, 225a), 317
 Palinek, G. J., 95(121b), 134
 Pande, K. G., 262(226), 263(226), 317
 Pang, M., 17(165), 57(165), 70(165), 87
 Papenroth, W., 271(93), 272(93), 312
 Paris, C., 16(61), 71(61), 84
 Parshall, G. W., 250(197, 227), 294(197, 227), 316, 317
 Parsons, T. D., 237(57), 260(57), 311, 318
 Pascal, P., 44(166), 67(166), 87
 Pasynkiewicz, S., 233(228a), 249(230), 253(229a), 298(228, 229), 317
 Paton, F. J., 210(175), 214(175), 223
 Pauling, L., 45(167), 47(167), 87
 Pauling, P., 99, 126(70), 133
 Paushkin, Ya. M., 295(266), 318
 Pauson, P. L., 99(15), 131
 Paxton, H. W., 204(145), 214(145), 223
 Peachy, S. J., 199(112), 207(112), 222
 Pearson, R. G., 255(183, 184), 256(183), 257(184), 306(183, 184), 315, 325(3), 332(28), 349, 350
 Pecile, C., 189(84), 221, 253(38), 299(38), 311
 Peddle, G. J. D., 36(70), 70(70), 85, 279 (79a) 285(79a), 288(79a), 312
 Pek, G. Yu., 324(52), 349(5), 349, 351
 Perkins, G. A., 270(173), 315
 Perkins, N. A., 238(45), 311
 Perret, A., 211(176), 215(176), 223
 Perrot, R., 211(176), 215(176), 223
 Pesci, L., 292(230a), 317
 Pestrikov, S. V., 323(43), 324(43), 325, 350, 351
 Peters, A. T., 173(19), 219(19), 220
 Petragrani, N., 272(50), 273(50, 51, 52, 53), 274(50, 52), 311
 Petrii, O. P., 241(179), 270(179), 315
 Petrov, A. D., 240(199, 202, 203, 204, 205, 206), 264(202, 203, 205, 206), 265 (206), 268(204), 316
 Petyunin, P. A., 232(230b), 317
 Pezarro, S., 78(147), 86
 Pfannstiel, K., 271(39), 311
 Pfeiffer, P., 8(168), 74(168), 87, 156(62), 159(70), 166, 167
 Pfohl, W., 262(231, 294), 317, 319
 Phillips, R. F., 186, 221
 Pickard, A. L., 153(59), 154(59), 155(59), 166
 Pierce, L., 40(169), 87
 Piesbergen, U., 201(123), 222
 Pikina, E. I., 8(170), 73(170), 87
 Piret, P., 121(149), 122(113, 122), 125 (113), 126(113), 134, 135
 Pischtschan, S., 46(133), 86, 148(47), 151 (55), 166
 Plant, S. G., 204(143), 205(143), 206(143), 223
 Polis, A., 11(171), 73(171), 87
 Pollak, J., 22(172), 87
 Pollard, F. H., 44(173), 54(66), 84, 87
 Poller, R. C., 8(174, 175), 25(175), 37 (175), 38(175), 47(175), 73(174), 78 (175), 79(175), 80(175), 81(175), 87, 139, 142(26), 160(80), 161(80, 87), 165(95), 165, 167, 174(28), 187(28), 197(28), 209(28), 210(28), 220
 Ponomarev, S. V., 241(179), 270(179), 289(178, 232), 296(233), 315, 317
 Pope, W. J., 199(112), 207(112), 222, 270 (180), 271(11), 310, 315
 Popkov, K. K., 283(292), 319
 Popova, Z. V., 84
 Porai-Koshits, M. A., 105(132), 134
 Porri, N., 99(6), 100(6), 101, 131, 134
 Portanova, R., 156(65), 166, 197(109), 222
 Post, H. W., 3(257), 13(115), 14(221), 25 (257), 29(257), 33(257), 51(115), 73 (221), 86, 88, 89, 212(182), 224, 289(176), 315
 Povarov, L. S., 5(158), 69(158), 71(158), 87
 Powell, A. R., 348(58), 351
 Powell, H. M., 186, 221
 Powell, J., 109(124), 134
 Prat, J., 270(234), 317
 Pratt, J. J., 50(51), 84
 Pratt, L., 96(77, 79), 105(78), 107(80), 133
 Price, T. S., 270(112), 313

Prieber, E., 99(71), 133
 Prince, M. I., 197(107), 199(107), 215(107), 222
 Pritchard, H. O., 45(176), 87
 Prokai, B., 234(149, 158, 167, 168), 236(149), 237(158, 168), 238(158), 239(158), 240(158), 243(149, 167), 247(169), 251(169), 253(169), 259(158), 261(158, 168), 278(169), 280(167), 285(167), 287(167), 288(149), 289(149, 169), 314, 315
 Prokhorova, A. A., 295(266), 318
 Puddephatt, R. J., 232(79b), 285(79b), 288(79b), 289(79b), 292(79b), 297(79b), 312
 Pump, J., 14(238), 195(99), 222
 Pyszora, H., 170(4), 178(39), 187(39, 70), 188(39), 194(70), 197(108), 198(39), 199(39), 208(4, 39, 161), 211(4), 219, 220, 221, 222, 223, 245(169a), 315

Q

Quane, D., 2(177), 87

R

Rabel, F. M., 241(235), 269(235), 317
 Raff, P., 197(105), 222
 Raiziss, G. W., 173(18), 204(18), 205(18), 206(18), 219(18), 220
 Ramachandran, J., 188(75), 221
 Randic, M., 97, 134
 Rao, C. N. R., 188(75), 217(196), 221, 224
 Raschig, F., 216(191, 192), 224
 Rathke, M. W., 255(235a), 302(235a), 317
 Razuvaev, G. A., 14(178), 87
 Redpath, C. R., 112(110), 134, 326(45), 350
 Rees, R. G., 143(29), 157(29), 166
 Reich, R., 201(119a), 222
 Reiche, A., 61(183), 73(183), 87, 216(187), 224
 Reichle, W. T., 8(179), 11(179), 12(180), 29(179), 70(180), 73(179, 180, 181), 80(179), 87, 164(93), 167, 177(35), 216(35), 217(33, 35, 194, 197), 220, 224, 233(236), 248(236), 317
 Reid, E. E., 2(182), 87, 292(81), 312

Reinert, K., 278(237), 280(237), 282(237), 287(237), 317
 Reinhardt, W., 8(222), 88
 Reinheckel, H., 244(238, 239), 247(238a), 253(238), 279(239), 280(239), 282(239), 287(239), 291(238a), 295(238a), 317
 Reinmuth, O., 232(160a), 248(160a), 251(160a), 252(160a), 315
 Reintjes, M., 295(118, 119), 313
 Renshaw, R. R., 270(240), 317
 Renson, M., 189(85, 86), 212(85), 221
 Reppe, W., 302(241), 303(241), 305(241), 317
 Reyhing, J., 178(41), 179(41), 188(41), 220
 Rich, A., 94(65), 133
 Richards, G. F., 327(2), 349
 Richards, J. H., 95(95), 133
 Richards, O. V., 174(24), 177(24), 197(24), 202(24), 211(24), 215(24), 217(24), 220
 Richards, R., 253(61c), 311
 Richards, R. E., 189(82), 213(82), 221
 Richter, P., 174(26), 200(117), 216(26, 117), 220, 222
 Rieber, M., 187(70), 194(70), 198(70), 221
 Riemschneider, R., 271(242), 317
 Rijkens, F., 2(184, 185), 45, 46(185), 47(185), 87
 Riley, H. L., 271(245), 272(245), 317
 Riley, R. F., 271(243, 244), 272(245), 317
 Ritter, A., 16(46), 18(46), 19(46), 22(46), 34(46), 52(46), 69(46), 71(46), 84, 174(26), 200(117, 118), 208(167), 216(26, 117), 220, 222, 223, 296(21), 310
 Robb, R. A., 142(25), 143(25), 165
 Robertson, G. B., 126(70), 133
 Robinson, G., 101, 109(117), 124(114, 117), 134
 Robinson, G. W., 340(61), 351
 Robinson, S. D., 108(126, 127), 109(124), 134, 276(245a), 317, 348(62), 351
 Robson, A., 101, 134
 Roch, J., 174(25), 206(25), 217(25), 220
 Rochow, E. G., 8(58, 92, 186), 25(186), 41(57), 45(19), 73(57, 58, 92), 83, 84, 85, 87, 138(2), 139(6), 146(2), 148(2), 150(2), 160(72, 79), 161(79), 165, 167,

172(11), 175, 199(11), 203(11), 210
(11), 212(184), 213(11), 217(11), 219,
220, 224
Roncucci, L., 143(27, 39), 156(27), 157
(27), 165, 166, 211(177), 224
Roper, W. R., 87
Rosenberg, S. D., 2(109), 22(109), 85, 138
(1), 141(1), 159(1, 71), 165, 167, 203
(135), 209(135), 213(135), 222
Ross, A., 160(74, 83), 161(83), 162(83), 167
Rosser, R. J., 270(156), 314
Rothermundt, M., 49(188), 74(188), 87
Rowe, J. M., 105(129), 127, 134
Rühlmann, K., 216(187), 224
Ruf, H., 9(204, 205, 206, 207), 21(204, 207),
25(204), 81(204, 207), 82(204, 205), 88
Ruidisch, I., 19(189, 190), 20(189, 190),
34(189, 190), 42(189, 190, 202), 69
(189, 190), 70(189), 71(189), 73(189),
81(190), 82(190), 87, 88, 216(193),
217(193), 224
Rule, C. K., 333(63), 351
Rundle, R. E., 100(69), 128, 130(49),
132, 133, 139(12), 165
Rushton, J., 204(143), 205(143), 206(143),
233
Russ, C. R., 291(245b), 317
Russell, D. R., 109(112), 111(112), 113
(75), 125(111), 126(111), 133, 134
Ruttinger, R., 321(66), 323(66), 324(66),
325(66), 326(66), 329(66), 344(66), 351
Rybakova, N. A., 60(191), 88

S

Sabel, A., 321(67), 323(67), 324(67), 329
(67), 330(67), 331(67), 332(67), 336
(67), 342(67), 345(67), 351
Saegusa, T., 249(93a), 250(93a), 312
Saing, M. B., 95(130), 134
Sandell, E. G., 328(72), 351
Sanderson, R. T., 88
Sasin, G. S., 11(195), 12(195), 14(194,
196), 26(195), 55(193, 195, 196), 56
(193, 194, 195), 60(195), 70(195), 88
Sasin, R., 10(193), 11(195), 12(195), 14
(194, 196), 26(195), 55(195, 196), 56
(194, 195), 60(195), 70(195), 88
Satgé, J., 17(143), 52(143), 86, 283(246),
287(246), 291(246), 317

Sato, H., 143(34), 150(34), 160(76), 164
(76), 166, 167
Saunders, B. C., 10(102, 150), 11(103),
12(150), 14(103), 23(102), 26(102),
57(102, 103, 150), 64(103), 85, 86,
207(156), 223
Savel'ev, A. O., 323(43), 324(43), 350
Saveleva, I. S., 262(211), 271(211), 316
Savina, L. A., 262(291), 319
Sawyer, A. K., 160(74), 167
Sayre, R., 44(197), 88
Schaeffer, R., 173(23), 174(23), 215(23),
220
Schaerer, U., 257(48c), 311
Scherer, O. J., 278(248), 279(248), 283
(248), 287(247), 317
Schick, R., 140(19), 165
Schlemper, E., 182(52, 53, 55), 184(52),
185(53, 55), 199(52, 55), 203(52), 220
Schlesinger, H. I., 237(57), 260(57), 311,
318
Schleyer, P. V. R., 183(59), 221
Schlimper, R., 89
Schmeisser, M., 8(199), 21(199), 22(198),
23(199, 200), 24(198), 59(199), 64
(199), 66(199), 71(198), 72(199),
80(199), 88
Schmidbaur, H., 42(201, 202), 88, 151(54),
166, 248(253), 249(249), 293(249, 251,
252, 253, 254), 318
Schmidt, E., 270(250), 318
Schmidt, K. H., 195(104), 222
Schmidt, M., 4(243, 244, 245, 246, 247, 248,
249, 250, 251, 252), 6(211), 9(204, 205,
206, 207), 14(203, 210, 213), 15(203,
208, 209), 18(215, 216, 217, 218, 219,
220), 19(189, 190), 20(215, 216, 217,
218, 219, 220), 21(203, 204, 207, 217),
23(215), 24(211, 244, 247, 248, 249),
25(204, 211, 213, 244, 247, 249), 26
(211, 242, 245, 249), 34(189, 190),
35(211), 37(216), 41(210, 214), 42
(189, 190, 246, 247, 248, 249, 250),
52(210), 54(219), 56(213), 57(203,
216), 64(203, 217), 69(189, 190, 210,
219), 70(189, 213, 215, 216, 219, 220),
71(189, 219), 72(213, 215, 216, 217,
220), 73(189, 203, 210), 74(243), 75
(243, 245, 246, 247, 249, 252), 76

- (242, 243, 244, 248, 250), 77(243, 244, 247, 248, 249, 251, 252), 78(249) 79 (244, 247, 248), 81(190, 204, 207, 208, 213), 82(190, 204, 205, 209, 215, 218, 219, 220), 83(220), 87, 88, 89, 162(89), 167, 216(193), 217(193), 224, 241(259), 248(253), 278(248), 279(248), 283 (248), 284(258), 287(247), 288(258), 291(258), 293(251, 252, 253, 254, 255), 318
- Schmitz-Dumont, O., 284(256, 257), 318
- Schneider, R., 99(71), 133
- Schneider, W. S., 239(286), 262(286), 319
- Schoening, F. R., L. 106(150), 135
- Schomaker, V., 46(212), 88, 101, 133
- Schramm, J., 208(167), 223
- Schrauzer, G. N., 124(131), 134
- Schubart, I., 174(25), 206(25), 217(25), 220
- Schuieler, E., 177(36), 179(36, 46), 189 (36, 46), 194(36), 208(46), 215(185a), 218(36, 46), 220, 224
- Schulte, H., 284(257), 318
- Schultz, R. G., 236(257b), 275(257a), 276(257b), 318
- Schumann, H., 14(203, 210, 213), 15(203, 208, 209), 18(215, 216, 217, 218, 219, 220), 20(215, 216, 217, 218, 219, 220), 21(217), 23(215), 25(213), 37(216), 41(210, 214), 52(210), 54(219), 56 (213), 57(203, 216), 64(203, 217), 69 (210, 219), 70(213, 215, 216, 219, 220), 71(219), 72(213, 215, 216, 219, 220), 73(203, 210), 18(208, 213), 82(203, 209, 215, 218, 219, 220), 83(220), 88, 162(89), 167, 241(259), 284(258), 288(258), 291(258), 318
- Schuster, R. E., 253(56), 299(56), 311
- Schwartz, W. T., Jr., 14(221), 73(221), 88
- Schwarz, R., 8(222), 88
- Schweizer, P., 248(215), 316
- Schwen, G., 206(151), 223
- Sedlmeier, J., 321(32, 66, 67), 323(66, 67), 324(32, 66, 67), 325(66), 326(66), 329 (32, 66, 67), 330(67), 331(67), 332(67), 336(67), 342(67), 344(66), 345(67), 350, 351
- Segler, R. C., 324(40), 326(40), 344(40), 350
- Seiber, R., 321(66), 323(66), 324(66), 325 (66), 326(66), 329(66), 344(66), 351
- Seip, R., 39(20), 40(20), 83
- Selwitz, C. M., 323(22), 345(21), 350
- Sessions, W. V., 15(126), 23(126), 26(126), 70(126), 86
- Sevdik, V. F., 105(132), 134
- Seyferth, D., 8(92, 224), 9(224), 10(223), 14(223), 47(229), 55(223), 73(92, 224), 85, 88, 156(63), 160(79), 161(79), 166, 167, 172(11), 174(30), 182, 195 (30, 56), 196(30, 56), 199(11), 203 (11, 30), 210(11), 212(30), 213(11, 30), 217(11), 219, 220
- Shapiro, H., 9(62), 23(62), 70(62), 84
- Sharkey, W. H., 174(29), 183(29), 194(29), 202(29), 207(29), 208(29), 220
- Shaw, B. L., 108(108, 126, 127), 109(124), 125(24), 132, 134, 275(177b), 276 (177b, 245a, 259a), 277(259a), 315, 317, 318 324(31), 326(31), 335(17, 18), 348(62), 350, 351
- Shaw, B. W., 120(118), 134
- Shchukarev, S. A., 328(64, 65), 351
- Shearer, H. M. M., 101(67), 107(67), 133
- Sheichenko, V. I., 268(200), 316
- Sheppard, N., 113(2), 131
- Shiba, T., 329(25), 332, 342(25), 343(25), 350
- Shier, G. D., 202(126a), 211(126a), 222
- Shimanouchi, T., 165(96), 167
- Shindo, M., 151(53), 166
- Shlenskaya, V. I., 328(7, 8), 349
- Shoemaker, D. P., 96(133), 125(157), 134, 135
- Shoemaker, V., 101, 181(64), 133
- Shul'ta, N. N., 329(48), 337(48), 342(48), 350
- Shur, V. B., 233(276a), 318
- Sieber, R., 321(67), 323(67), 324(67), 329 (67), 330(67), 331(67), 332(67), 336 (67), 342(67), 345(67), 351
- Siebert, H., 47(225), 88
- Sisler, H. H., 249(6), 251(6), 293(6), 297(6), 310
- Skell, P. S., 240(260), 264(260), 318
- Skinner, H. A., 45(176), 87, 148(48), 154(48), 166
- Sliwa, E., 249(230), 317
- Slotta, K. H., 201(122), 222

- Sly, W. G., 116(134), 134
 Smaller, G. T., 95(135), 134
 Smart, G. R. N., 8(90), 24(90), 25(90), 52(90), 85
 Smidt, J., 321(32, 66, 67), 322(68), 323(67, 68), 324(32, 66, 67, 68), 325(66), 326, 329(32), 330(67), 331, 332, 336(67), 342(67), 344(66), 345(67), 350, 351
 Smiles, S., 22(86), 85
 Smith, A. C., 8(92), 73(92), 85, 172(11), 199(11), 203(11), 210(11), 213(11), 217(11), 219
 Smith, A. C., 160(79), 161(79), 167
 Smith, A. E., 105(136), 111(136), 134
 Smith, A. S., 210(175), 214(175), 223
 Smith, D. L., 101, 102(47), 118(48), 124(137), 132, 134
 Smith, G. H., 99(15), 131
 Smith, H. D., Jr., 280(137), 281(137), 287(137), 314
 Smith, J. A. S., 112(110), 134, 326(45), 350
 Smith, L. M., 204(143), 205(143), 206(143), 223
 Smith, P. W., 180(78), 188(78), 221
 Smythe, L. E., 9(80), 24(80), 29(80), 36(80), 69(80), 85
 Soborovskii, L. Z., 270(44), 311
 Söderbäck, E., 201(124), 208(160), 211(124), 222, 223
 Sönke, H., 294(186a), 306(186a), 316
 Soszynska, E., 298(229), 317
 Sowerby, D. B., 178(42), 188(42, 79), 212(42), 220, 221
 Spada, A., 205(150), 214(150), 223
 Sparke, M. B., 323(69), 324(69), 346(69), 351
 Spatz, S. M., 224
 Spector, M. L., 323(71), 324(71), 351
 Spiridonova, T. G., 270(44), 311
 Sprague, M. J., 178(43), 189(43), 220
 Srivastava, T. N., 9(226), 35, 70(226), 88, 209(174), 213(174), 217(193a), 223, 224
 Stacey, G. J., 11(103), 14(103), 57(103), 64(103), 85
 Stamm, W., 172(14), 173(14), 200(14), 209(14), 210(14), 219
 Steinkopf, W., 174(25), 206(25, 151), 213(184a), 217(25), 220, 223, 224
 Stephenson, T. A., 348(58), 351
 Stern, D. R., 259(261), 260(261), 318
 Stern, E. W., 323(71), 324(70, 71), 345, 351
 Sternbach, B., 46(227), 88
 Sternberg, H. W., 116(81, 138), 133, 134, 242(112a), 275(112a), 313
 Stetter, J., 3(114), 86
 Stevenson, D. P., 46(212), 88
 Stiegler, H. W., 270(174), 315
 Stienstra, F. J., 8(37, 38, 39, 40, 41), 25(37), 33(39), 39(40), 66(37, 38, 40, 41), 67(39, 41), 78(39, 41), 84
 Stone, F. G. A., 2(228), 47(229), 88, 126, 135, 242(282, 283, 284), 274(282, 283, 284), 275(282, 283, 284), 319
 Straley, J. M., 244(109a), 313
 Strametz, H., 292(271), 318
 Strarovskii, O. V., 95(141), 99, 135
 Strommen, D. P., 178(37), 179(37), 187(37), 197(37), 199(37), 209(37), 210(37), 213(37), 216(37), 217(37), 220
 Struchov, Yu. T., 95(98, 99, 141, 142, 143, 144), 99, 134, 135, 266(277), 267(277), 268(277), 271(262), 318
 Stukan, R. A., 165(94), 167
 Stump, D. D., 263(265b), 318
 Styann, G. E., 241(72), 270(72), 271(72), 312
 Subramanian, R. V., 348(42), 350
 Sugden, T. M., 187(72a, 73), 191(73), 221
 Sugita, K., 164(91), 167
 Sujishi, S., 85, 196(101, 102), 222
 Sultzaberger, J. A., 204(139), 206(139), 214(139), 223
 Summers, L., 2(142), 86, 203(137), 204(137), 210(137), 213(137), 219(137), 222
 Sumner, C. G., 116(145), 124(145), 131(145), 135
 Sundaram, A. K., 328(72), 351
 Sundermeyer, W., 173(22), 216(22, 188, 189), 220, 224
 Surtees, J. R., 249(195), 316
 Sustmann, R., 216(191, 192), 224
 Sutton, L. E., 39(253), 89, 148(48), 154(48), 166

- Sutton, P. W., 125, 132
 Suzdal'nitskaya, Yu. V., 329(46, 47), 337
 (46, 47), 342(46, 47), 350
 Svátek, E., 180(49), 220
 Svatos, G. F., 337(73), 351
 Swallow, A. G., 126(146), 135
 Symes, W. R., 245(80a), 250(80), 296
 (80, 80a), 312
 Syrkin, Ya. K., 323(54), 324(51, 54, 80),
 325(56), 326(54), 329(78, 79, 81), 330
 (54, 55), 333(81), 334(54, 57, 81),
 336(54, 55, 56, 57, 79, 81), 337(56),
 344(54), 346(54), 351, 352
- T**
- Tafel, J., 8(230), 73(230), 88
 Taikova, N. K., 60(191), 88
 Takegami, Y., 307(263, 264), 318
 Talalaeva, T. V., 8(170), 73(170, 231), 87,
 89
 Tanaka, J., 301(265), 318
 Tanaka, T., 143(28, 31, 38, 41), 147(46),
 150(52), 155(28), 157(28), 158(31),
 160(84), 161(84), 165, 166, 167
 Tanata, K., 329(50), 342(50), 351
 Tandon, S. K., 9(226), 35, 70(226), 88,
 209(174), 213(174), 223
 Tarantelli, T., 189(84), 221
 Tate, J. M., 7(49), 8(49), 16(49), 57(49),
 84, 139(8), 143(9), 165
 Taube, H., 339(74), 341, 349, 351
 Taylor, R., 40(75), 41(75), 85, 187(72), 221
 Tchakirian, A., 11(232), 44(166), 67(166),
 82(232), 87, 89
 Teer, P. A., 73(77), 85
 Teichner, S. J., 292(207), 316
 Templeton, D. H., 94(82), 129(159), 133,
 135, 328(75), 351
 Teramoto, K., 329(76), 333(76), 351
 Thayer, J. S., 140(22, 23), 165, 170(3),
 171(7, 8), 172(8, 13), 176(3), 177(3),
 178(3, 37, 44), 179(8, 13, 37), 180
 (13, 44), 187(37), 191, 192(13), 194
 (13), 198(3, 8, 103), 197(37), 199
 (13, 37), 209(37), 210(37), 213(37),
 215(3), 216(3, 7, 8, 13, 37, 44), 217
 (3, 8, 13, 37, 44), 218(44), 219(44),
 219, 220, 222
 Thirius, K., 89
 Thorn, K. F., 18(215, 216, 217, 218, 219,
 220), 20(215, 216, 217, 218, 219, 220),
 21(217), 23(215), 37(216), 54(219),
 57(216), 64(217), 69(219), 70(215, 216,
 219, 220), 71(219), 72(215, 216, 217,
 220), 82(215, 218, 219, 220), 88
 Thomas, A. B., 139(6), 165
 Thomas, R. M., 209(169), 223
 Thorsteinson, E. M., 306(185), 315
 Thyret, H., 124(131), 134
 Tieckelmann, N., 3(257), 25(257), 29(257),
 33(257), 89
 Tilley, B. P., 234(71, 149), 236(149), 243
 (71, 149), 244(71), 247(170), 251(170),
 253(170), 281(71, 170), 286(71), 288
 (149), 289(149, 170), 291(170), 297
 (170), 312, 314, 315
 Tilney-Bassett, J. F., 275(265a), 318
 Tipper, C. F., 112(147), 135
 Titmus, P. L., 263(265b), 318
 Tobias, R. S., 143(30, 32, 36, 37), 144
 (30), 145(30), 157(30), 158(30, 32),
 166
 Todd, L. J., 171(5), 215(5), 219, 301(146),
 314
 Tomaszewski, A. J., 314
 Tomaszewski, B., 246(143, 144), 298(228),
 317
 Topchiev, A. V., 5(158), 43(234), 69(158,
 234), 71(158, 234), 87, 89, 295(266),
 318
 Toporcer, L. H., 240(280), 264(280), 319
 Treichel, P. M., 242(283, 284), 274(283,
 284), 275(283, 284), 308(266a), 319
 Trommet, A., 321(32), 324(32), 329(32),
 350
 Trotter, J., 95(109, 135, 148), 134, 135,
 146(45), 166, 182(54), 185(54), 199
 (54), 220
 Trueblood, K. N., 95(130), 134
 Trukhtanow, V. A., 165(94), 167
 Truter, M. R., 101, 108(108), 126(146),
 134, 135
 Tsai, J. S., 270(62, 63, 64), 275(62), 311
 Tsang, W. S., 270(62, 64), 275(62), 311
 Tsao, M., 340(77), 351
 Tseng, Chao-Lun, 269(267), 318
 Tung, Shih-Hua, 269(267), 318

Turco, A., 253(38), 299(38), 311
 Turner, E. B., 271(145), 314
 Turner, J. J., 42(76), 85
 Turner, L., 323(69), 324(69), 346(69), 351
 Tyfield, S. P., 48(12), 83

U

Uden, P. C., 44(173), 87
 Ueeda, R., 143(38), 160(84), 161(84), 166, 167
 Uhlenbranck, H., 200(118), 222
 Urenovitch, J. V., 174(27), 202(27), 203(27), 207(27), 209(168), 220, 223
 Urry, G., 171(6), 216(6), 219, 237(57), 260(57), 311, 318
 Uttech, R., 106(59), 109(59), 111(59), 133
 Uvarova, N. G., 345(4), 349

V

Valentine, J., 99(15), 131
 Vallarino, L. M., 334(19, 20), 350
 Vallender, H. W., 270(136), 314
 van der Kerk, G. J. M., 2(148, 149, 161, 185), 17(162), 45, 46(185), 47(185), 70(149, 161, 162), 86, 87, 140(13, 14, 21), 149(50), 165, 166, 199(113, 114), 200(119), 217(113, 119), 222
 Vangindertaelen, A., 7(258), 23(258), 29(258), 68(258), 89
 van Meersche, M., 121(149), 122(113, 122), 125(113), 126(113), 134, 135
 van Niekerk, J. N., 106(150), 135
 Van Wazer, J. R., 30(155, 155a), 42(155a), 73(155), 81(155), 87
 Vargaftik, M. N., 323(54), 324(53, 54, 80), 325(56), 326(54), 329(78, 79, 81), 330(54, 55), 333(81), 334(54, 57, 81), 336(54, 55, 56, 57, 79, 81), 337(56), 344(53, 54), 346(54), 347(53), 348(53), 351, 352
 Vasta, J. A., 10(28), 35(28), 54(28), 84, 194(92), 221
 Venanzi, L. M., 189(82), 213(82), 221, 334(19, 20), 350
 Ventura, J. J., 160(82, 83), 161(82, 83), 162(83), 167
 Verity-Smith, H., 2(235), 50, 89

Vetter, H.-J., 237(269), 279(269), 292(269, 270, 271), 318
 Vilkov, L. V., 266(277), 267(277), 268(277), 318
 Vlcek, A. A., 293(272), 318
 Vogel, H., 271(39), 311
 Vol'pin, M. E., 233(276a), 318, 240(273, 275), 241(172, 275, 275a), 263(276), 265(275), 266(276, 277), 267(172, 274, 276, 277), 268(277), 274(273), 315, 318
 von Grosse, A., 172(12), 201(125), 204(140), 206(140), 207(159), 211(125), 215(12), 219, 222, 223
 Vorlander, D., 5(236), 89
 Voronkov, M. G., 211(180), 212(180), 224, 232(177a), 233(177a), 315

W

Wada, M., 140(24), 148(49), 151(53), 154(24), 155(61), 156(24, 66), 158(66), 160(75, 78, 84), 161(75, 78, 84), 162(75), 163(24, 75, 78), 165, 166, 167, 188(80, 81), 192(89), 197(80), 198(89), 213(80, 81), 221
 Wade, K., 244(64a), 253(150a), 298(150, 177), 311, 314, 315
 Wakefield, B. J., 233(277a), 319
 Walaschewski, E. G., 204(141), 213(141), 223
 Walker, D. F., 204(139), 206(139), 214(139), 223
 Walker, S. M., 237(59), 260(59), 311
 Wampler, D. L., 130(23), 131(23), 132
 Wannagat, U., 6(237), 14(238), 41(237), 42(237), 76(237), 89, 195(99), 222
 Ware, J. C., 237(59), 270(240), 317
 Wartik, T., 260(291a), 319
 Washburn, R. M., 216(192a), 217(192a), 224
 Watanabe, Y., 307(263, 264), 318
 Waterson, K. F., 275(278), 319
 Watt, G. W., 328(75), 351
 Webb, N. C., 95(151), 135
 Webster, D. E., 138(2), 140(15, 17), 146(2), 148(2), 150(2), 153(15), 165
 Weed, E. D., 328(82), 337(82), 352
 Wegun, P. A., 129(84), 133
 Wei, C. H., 129, 131(51), 132

- Weingarten, H., 258(278a), 319
 Weiss, E., 99, 114(89), 122(153), 133, 135
 Weiss, G., 209(169), 223
 Weiss, J., 340, 341(83), 352
 Weiss, K., 197(107), 199(107), 215(107), 222
 Wells, A. F., 45(239), 89, 185(61), 191, 221
 Wender, I., 3(140), 8(140), 51(140), 86, 116(81, 138), 133, 134, 242(112a), 275(112a), 313
 Wenham, A. J. N., 323(69), 324(69), 346(69), 351
 Werner, H., 337(27), 350
 West, R., 8(92), 24(240), 46(241), 73(92), 85, 89, 140(22), 165, 171(7, 8), 172(8, 13), 179(8, 13), 180(13), 191, 192(13), 194(13), 196(8, 103), 199(13), 216(7, 8, 13), 217(8, 13), 219, 220, 222, 241(235), 263(279), 269(235), 317, 319
 Westlake, A. H., 158(67), 167
 Weyenberg, D. R., 240(280), 246(280), 319
 Weyer, K., 248(293), 249(293), 293(293), 319
 Whatley, L. S., 46(241), 89
 White, D. G., 160(76), 164(76), 167
 White, R. F. M., 160(77), 161(77), 162(77), 167
 White, W. B., 188(77), 221
 Whiting, M. C., 245(3), 310
 Wiberg, E., 173(17), 215(17), 220
 Wiberg, N., 195, 216(190, 191, 192), 222, 224
 Wildmaier, I., 178(40), 186(40), 220
 Wieber M., 4(243, 244, 245, 246, 247, 248, 249, 250, 251, 252), 6(211), 24(211, 244, 247, 248, 249), 25(211, 244, 247, 249), 26(211, 242, 245, 249), 35(211), 42(246, 247, 248, 249, 250), 74(243), 75(243, 245, 246, 247, 249, 252), 76(242, 243, 244, 248, 250), 77(243, 244, 247, 248, 249, 251, 252), 78(249), 79(244, 247, 248), 88, 89
 Wieden, H., 296(21), 310
 Wieland, H., 270(281), 319
 Wildner, O., 197(105a), 222
 Wilford, J. B., 126, 135, 242(282, 283, 284), 274(282, 283, 284), 275(282, 283, 284), 319
 Wilhelm, I., 293(255), 318
 Wilke, G., 108, 135, 239(285, 286), 262(285, 286), 319
 Wilkes, G. R., 129(96), 133
 Wilkins, C. J., 39(253), 87, 89, 156(64), 166
 Wilkinson, G., 94(156), 96(77, 79), 105(78), 107(80), 117(11), 131, 133, 135, 275(112b, 278), 313, 315, 319, 348(58), 351
 Wilkinson, G. R., 187(72), 221
 Wilkinson, I. F., 214(185), 224
 Willcockson, G. W., 259(287), 260(287), 279(30), 281(30), 286(30), 310, 319
 Willemsens, L. C., 2(254), 89
 Willey, G. R., 46(13), 83
 Williamson, J. B., 323(29), 350
 Willis, C. J., 296(147a), 314
 Wilmarth, W. K., 340(77), 351
 Wilson, F. C., 125(157), 135
 Wilson, V. K., 189(83), 207(158), 210(158), 214(158), 221, 223
 Wing, R. M., 125, 132
 Winstein, S., 232(161), 240(161), 262(226), 263(226), 315, 317
 Witte, H., 253(131, 132, 133, 134), 299(131, 132), 300(132, 133), 301(133), 314
 Wittenberg, D., 16(256), 17(91, 255), 25(91, 255), 34(91, 255), 52(255, 256), 71(256), 85, 89
 Wittig, G., 197(105), 222, 249(288), 319
 Wojcicki, A., 235(19, 288a), 293(19, 117a, 288a, 288b), 310, 313, 319
 Wolinski, L., 3(257), 25(257), 29(257), 33(257), 89
 Wong, C. H., 96(158), 135
 Wood, D. C., 257(111b) 306(111b), 313
 Wood, J. K., 206(152), 223
 Wood, J. S., 98(40), 99(40), 132
 Woods, L. A., 237(101a, 108a), 253(109b), 312, 313
 Woodward, F. N., 270(136, 156), 314
 Woodward, L. A., 40(75), 41(75), 85, 187(72), 221
 Wooley, B. L., 313
 Wotiz, J. H., 116(81, 138), 133, 134, 242(112a), 275(112a), 313
 Wright, C. M., 159(69), 167
 Wright, D., 309(288c), 319
 Wright, G. F., 313

Wu, T. C., 16(256), 52(256), 71(256), 89
 Wunsch, G., 13(44), 51(44), 84
 Wuyts, Y., 7(258), 23(258), 29(258), 68
 (258), 89
 Wynne-Jones, W. F. K., 332(85), 352

Yoshida, Z., 297(289), 319
 Young, A. R., 197(105b), 199(105b), 202
 (105b), 222
 Young, D. C., 129(84), 133
 Young, R. V., 253(106a), 313

Y

Yakubovich, A. Ya., 73(259), 89
 Yale, A. L., 207(157), 214(157), 223
 Yamasaki, K., 5(163), 21(163), 39(261),
 72(163), 87, 89
 Yang, M. T., 245(82b), 307(82b), 312
 Yanovskii, D. M., 84
 Yarsley, V. E., 206(153), 223
 Yasuda, K., 147(46), 151(56, 57), 153(157),
 154(58), 163(56), 164(92), 166, 167
 Yasuda, M., 143(36), 166
 Yen, T. M., 96(158), 135
 Yokoi, M., 5(163), 21(163), 39(260, 261),
 72(163), 87, 89
 Yokokawa, C., 307(263, 264), 318

Z

Zachariasen, W. H., 47(262), 89
 Zado, F., 291(111a), 313
 Zahradnik, R., 180(49), 220
 Zaitseva, N. A., 73(231), 89
 Zakharkin, L. I., 248(290), 262(291), 319
 Zalkin, A., 129(159), 135
 Zeldin, M., 260(291a), 319
 Zhinkin, D. Ya., 283(292), 319
 Ziegler, K., 248(293), 249(293), 262(294),
 293(293), 319
 Zilberman, E. W., 60(191), 88
 Zimmer, H., 203(136), 222
 Zintl, E., 39(263), 89
 Zobel, T., 44(16), 83

Subject Index

A

- Acetaldehyde from ethylene, 321–352
- Acetylenes, *see* Alkynes
- Addition reactions, *see also* Insertion reactions
 - 1,1-addition, 230–232, 253–257
 - 1,2-addition, 226–230, 237–253
 - 1,4-addition, 227, 230, 237–253
- Alkenes, insertion reactions, 258–277
 - Group III elements, 258–263
 - Group IV elements, 263–270
 - Group V elements, 270–271
 - Group VI elements, 271–274
 - transition metals, 274–277
- Alkyl-transition metal complexes, 125–128
- Alkynes
 - insertion reactions, 258–277
 - Group III elements, 258–263
 - Group IV elements, 263–270
 - Group V elements, 270–271
 - Group VI elements, 271–274
 - reactions with metal carbonyls, structures of products, 114–125
 - metallo-ring systems, 120–124
 - non-polymerized ligands, 116–120
 - polymerized ligands, 124–125
- Allyl complexes
 - structure and bonding, 105–112
 - π into σ conversion, 109
- Aluminum compounds, alkyne insertion, 239
- Arene complexes, structures, 98–100
- Azides, *see also* Pseudohalides
 - properties, 215–217

B

- Bonding
 - in metal complexes with arenes, 98–100
 - with conjugated diolefins, 100–105
 - with cyclic conjugated ligands, 94–100
 - with π -cyclopentadienyl groups, 94–98
- in pseudohalides, 181–193
- in silicon compounds, 45

Boron compounds

- complexes with metal carbonyls, 129
- reactions with alkenes and alkynes, 237–239

C

- Cacodyl cyanide, 170
- Carbon monoxide, insertion reactions, 302–305
 - intramolecular insertion, 306–309
- Carbonylation, 230–231
- Carbonyl compounds, insertion, 228–231, 247–248, 291–292
- Conjugated diolefin complexes, structures, 100–105
- Cyanates, *see also* Pseudohalides
 - properties, 208–210
- Cyanide, *see also* Pseudohalides
 - properties, 201–207
- Cyclopentadienone as ligand, 101–104
 - structure, 102
- π -Cyclopentadienyl complexes, structures, 94–98
- Cyclopropane complexes, structure and bonding, 112–114

D

- Duroquinone complexes, 124

E

- Electron diffraction
 - organosilicon pseudohalides, 192
 - silicon-sulfur compounds, 39
- Ethylene, oxidation to acetaldehyde with
 - palladium chloride, 321–352
 - in aqueous media, 323
 - mechanism, 330–339
 - deuteration studies, 320
 - kinetics, 329
 - in non-aqueous media, 324, 343–346
 - mechanism, 346–349
 - reaction in presence of copper(II) salts, 339–343

F

- Ferrocene, structure, 94
- Fluorocarbon complexes, structures of, 125-128
- Fulminates, *see also* Pseudohalides properties, 218

G

- Germanium
 - organoselenium derivatives, 82
 - organosulfur derivatives, 52-54, 59, 65, 67, 69, 71-74, 76-78, 80-81
 - organotellurium derivatives, 82
- Gold, cyanide derivatives, 186
- Group IV compounds, reaction with alkenes and alkynes, 240-242
- Group IV organoselenium compounds, 81-83
- Group IV organosulfur compounds, 1-92
 - action of heat, 21-22
 - alkali metal derivatives, 18-21
 - bond parachors, 43
 - π -bonding, 47-48
 - cyclic derivatives, 3-6
 - electron diffraction, 39
 - infrared and Raman spectroscopy, 40-41
 - group frequencies, 41
 - microwave spectra, 40
 - NMR spectra, 42
 - oxidation, 23-24
 - properties, 51-83
 - reactions with amines, 26
 - with bases, 24-26
 - with covalent halides, 27-34
 - with hydrogen halides, 26
 - with sulfur, 22
 - with thiols, 26
 - reduction, 24
 - syntheses, 3-23
 - from alkali metal compounds, 19-21
 - by cleavage of metal-carbon bonds, 14-15
 - metal-metal bonds, 15-16
 - from halides, 3-10
 - from hydrides, 16
 - from nitrogen and phosphorus compounds, 13-14
 - from oxides, 10-12
- X-ray studies, 38-39

- Group IV organotellurium compounds, 81-83
- Group V compounds, reaction with alkenes and alkynes, 242

H

- Heterocyclic compounds
 - metallo-ring systems, 122-124
 - sulfur systems
 - reactions, 26, 28, 30-33, 35-37
 - synthesis, 4-7, 15

I

- Infrared spectra
 - Group IV organosulfur derivatives, 41
 - organotin compounds, 146-158
 - determination of configuration, 145
 - pseudohalogen compounds, 178-179
- Insertion reactions, 225-319
 - aldehydes, 230, 249-251, 294-296
 - alkenes, 227, 237, 258-277
 - alkynes, 227, 237, 258-277
 - allenes, 227, 275-276
 - carbenes, 231
 - carbodiimides, 228, 243-247, 288-289
 - carbon dioxide, 228, 247-248, 291
 - carbon disulfide, 228, 247-248, 291-292
 - carbon monoxide, 230-231, 254-257, 302-309
 - carbonyl sulfide, 228, 247-248, 291
 - diketene, 228, 243-247, 290
 - general considerations, 232-236
 - isocyanates, 227, 243-247, 278-287
 - isonitriles, 231, 253-254, 299-301
 - isothiocyanates, 228, 243-247, 287
 - ketenes, 228, 243-247, 289
 - ketones, 230, 249-251, 294-296
 - metals, 231
 - nitrene, 231
 - nitriles, 230, 252-253, 298
 - nitrogen oxides, 230, 251-252, 297
 - nitro and nitroso compounds, 230, 251-252, 297
 - nonmetals, 231
 - oxygen, 230
 - selenium trioxide, 230, 248-249, 293
 - sulfur oxides, 230, 248-249, 293
 - N*-thionylamides, 229, 247-248, 292

- Isocyanates, *see also* Pseudohalides
properties, 208–210
Isocyanides, *see also* Pseudohalides
properties, 182–186
Isoselenocyanates, *see also* Pseudohalides
properties, 218–219
Isothiocyanates, *see also* Pseudohalides
properties, 211–214

L

- Lactone-cobalt carbonyl complex, structure, 124
Lead
 organoselenium compounds, 83
 organosulfur compounds, 57–58, 64, 70, 72–73, 80
 organotellurium compounds, 83
Lewis acids and bases, adducts with organo-metallic pseudohalides, 196–197

M

- Metal carbonyl derivatives, structures, 128–131
Metal-metal bonds, cleavage by sulfur compounds, 15–16
Metallo-cyclopentadiene complexes, 120–122
Metallo-ring systems, 122–124
Microwave spectra
 dimethyl sulfide, 40
 organosilicon pseudohalides, 191

N

- Nickelocene, structure and reactivity, 119
Nuclear magnetic resonance (NMR), Group IV organosulfur derivatives, 41–42

O

- Organometallic pseudohalides, 169–224
Organoselenium derivatives of Group IV, 81–83
Organostannoxanes, 159–165
 polymeric organotin oxides, 164–165
 structures, 161–164
Organosulfur derivatives of Group IV, 1–92

- Organotellurium derivatives of Group IV, 81–83
Organotin compounds, 137–167
 bonding, 144–145
 configuration, 139–144
 determination by infrared spectroscopy, 145
 infrared spectra, 146–158
 structural considerations, 137–167
 5-coordinate, 140–142
 6-coordinate, 142–143
 7-coordinate, 144

P

- Palladium chloride, in oxidation of ethylene to acetaldehyde, 321–352
 complexes in solution, 323–324, 328–329
 effect of copper(II) salts, 339–343
Palladium-olefin complexes, 324–326
 structure, 326–328
Pseudohalides, organometallic, 169–224
 adducts with Lewis acids and bases, 196–197
 bonding, 189–193
 chemical properties, 193–200
 displacement reactions, 194–195
 exchange reactions, 193–194
 infrared spectra, 177–179
 polymers, 198–199
 properties
 azides, 215–217
 fulminates, 218
 (iso)cyanates, 208–210
 (iso)cyanides, 201–207
 (iso)selenocyanates, 218–219
 (iso)thiocyanates, 211–214
 reactions of pseudohalide group, 199–200
 solvolysis, 193
 structural isomerism, 181–189
 resonance, 190
 synthesis, 171–174
 by metathesis, 171–172
 from pseudohalogen derivatives, 172–173
 by pyrolysis, 174
 thermal stability, 175–177
 trends in properties, 175
 ultraviolet spectra, 179–181

R

Ring opening by insertion reactions, 230

S

Selenium trioxide insertion reactions, 293

Selenocyanates, *see also* Pseudohalides
properties, 218–219

Silicon compounds

π -bonding, 45–47

isocyanides, 182–183

organoselenium derivatives, 81

organosulfur derivatives, 51–52, 59, 64,
66–67, 69, 71, 72, 74–76, 80

organotellurium derivatives, 81

Spirocyclic sulfur systems, 7, 10, 12

Structural parameters of organometallic
cyanides, 182

Structures of organometallic complexes,
93–135

acetylene-metal carbonyl complexes, 114–
125

perfluorocyclohex-1-yn-3-ene dicobalt
hexacarbonyl, 117

$\text{Co}_2(\text{CO})_4(\text{HC}_2\text{H})(\text{HC}_2\text{Bu})_2$, 109

$\text{Co}_2(\text{CO})_6(\text{Ph}_2\text{C}_2)$, 116

$\text{Co}_2(\text{CO})_8(\text{HC}_2\text{H})$, 125

$\text{Co}_4(\text{CO})_{12}(\text{Et}_2\text{C}_2)$, 118

$\text{Fe}_2(\text{CO})_6(\text{Ph}_2\text{C}_2)$, 121

$\text{Fe}_2(\text{CO})_6(\text{HC}_2\text{H})_3$ (two isomers), 122–
123

$\text{Fe}_2(\text{CO})_6(\text{PhC}_2\text{H})_3$, 123

$\text{Fe}_3(\text{CO})_8(\text{Ph}_2\text{C}_2)_2$ (black isomer), 120

$\text{Fe}_3(\text{CO})_8(\text{Ph}_2\text{C}_2)_2$ (violet isomer), 117

$\text{H}_2\text{Fe}_2(\text{CO})_8(\text{Me}_2\text{C}_2)$, 121

allyl complexes, 105–112

π -allyl palladium acetate, 106

π -allyl palladium chloride, 106

bis(methallyl)nickel, 106

cyclooctadienyl palladium acetylaceto-
nate, 108

dodeca-2,6,10-triene-1,12-dienyl
ruthenium chloride, 108

ethoxytetraphenylcyclobutenyl palla-
dium chloride, 107

exo-ethyltetramethylcyclobutenyl- π -
cyclopentadienylnickel, 107

$\text{Co}_2(\text{CO})_4(\text{HC}_2\text{Bu})_2(\text{C}_2\text{H}_2)$, 109

$\text{Pd}(\text{C}_3\text{H}_4\text{Me})\text{P}(\text{C}_6\text{H}_5)_3\text{Cl}$, 109–110

Structures of Organometallic complexes

—*continued*

arene complexes, 98–100

$(\text{C}_6\text{H}_6\text{PdAl}_2\text{Cl}_7)_2$, 99

conjugated diolefin complexes, 100–105

π -cyclopentadienyl-hexakis(trifluoro-
methyl)benzene-rhodium, 100

cyclopentadienone ligand, 102

π -cyclopentadienyl complexes, 94–98

ferrocene, 94

nickelocene, 119

nickelocene-dimethyl acetylenedicar-
boxylate adduct, 119

ruthenocene, 94

$(\pi\text{-C}_5\text{H}_5)_2\text{MoH}_2$, 96

cyclopropane complexes, 112–114

$(\text{C}_3\text{H}_6)\text{PtCl}_2\text{py}_2$, 113

duroquinone-cyclooctadiene-nickel, 124

fluorocarbon complexes, 125–128

perfluorocyclohex-1-yn-3-ene dicobalt
hexacarbonyl, 117

$(\text{CF}_3)_6\text{C}_6\text{Rh}(\pi\text{-C}_5\text{H}_5)$, 100

lactone-cobalt carbonyl complex, 125

metal carbonyl derivatives, 128–131

$[\text{HFe}_3(\text{CO})_{11}]^-$, 128

$\text{HMn}_3(\text{CO})_{10}(\text{BH}_3)_2$, 129

$(\pi\text{-B}_9\text{C}_2\text{H}_{11})\text{Fe}(\pi\text{-C}_5\text{H}_5)$, 129

metallo-ring systems, 120–124

$\text{Fe}_2(\text{CO})_6(\text{Ph}_2\text{C}_2)$, 121

$\text{Fe}_2(\text{CO})_6(\text{C}_2\text{H}_2)_3$, 123

$\text{Fe}_2(\text{CO})_6(\text{PhC}_2\text{H})_3$, 123

$\text{Fe}_3(\text{CO})_8(\text{Ph}_2\text{C}_2)$ (black isomer), 120

$\text{H}_2\text{Fe}_2(\text{CO})_8(\text{Me}_2\text{C}_2)$, 121

osmacyclopentadiene complex, 122

trimethylgermanium cyanide, 184

trimethyltin cyanide, 185

trimethyltin fluoride, 147

trimethyltin formate, 149

ylid-platinum complex, 113

Sulfur oxides, insertion reactions, 230,
248–249, 293

T

Thallium(III) acetate, reaction with olefins,
240

Thiocarbonyl compounds, insertion reac-
tions, 291–292

Thioycanates, *see also* Pseudohalides

properties, 211–214

Tin isocyanides, 184–185

Tin

organoselenium derivatives, 82

organosulfur derivatives, 54–57, 59–64,
65, 67–68, 70, 72, 73, 74, 78–80, 81, 82

organotellurium derivatives, 82

Trimethyltin compounds, 146–148, 151–
156

U

Ultraviolet spectra, pseudohalides, 180–181

V

Vaska complex, 232

Y

Ylid complex, structure, 113

Cumulative Subject Index:

Volumes 1-5

A

Acyl cobalt tetracarbonyls, **4**, 243-266
 Alkali-metal adducts of aromatic hydrocarbons, **2**, 115-152
 Alkali-metal cyclopentadienides, **2**, 369-379
 Alkali-metal metal carbonyl derivatives, **2**, 157-250
 Alkenes, insertion reactions, **5**, 258-277
 Alkylboranes, **2**, 284-287; **3**, 294-295, 300-301
 Alkyl cobalt tetracarbonyls, **4**, 243-266
 Alkyl-metal compounds, **5**, 125-128
 Alkyne-metal carbonyl complexes, **1**, 37-43; **5**, 114-125
 Alkynes, reactions, **1**, 3-4, 62-65, 200; **2**, 3-9; **5**, 258-277
 π -Allyl complexes, **2**, 41-43, 330-356; **3**, 71-91; **4**, 247-250, 260-262, 357-384; **5**, 105-112
 σ -Allyl complexes, **2**, 326-329
 Aluminum compounds, **3**, **5**; **5**, 239
 Ammine complexes, **3**, 197-247
 Anionic metal carbonyls, **2**, 157-250
 Arene complexes, **1**, 291-302; **3**, 150-154; **5**, 98-100
 Arene metal carbonyls, **1**, 299-301; **3**, 211
 Aromatic hydrocarbon anions, **2**, 118-152
 Aromatic systems, conjugate addition of Grignard reagents to, **1**, 221-237
 Arsenic compounds, **4**, 145-229
 Arsine complexes, **3**, 204-251
 Azides, organometallic, **5**, 215-217
 Azulene complexes, **3**, 107-113; **4**, 366-368

B

Bicycloheptadiene complexes, **1**, 18-19, 28
 Bicyclooctadiene complexes, **4**, 381-382
 Bis(acrylonitrile) nickel, **2**, 14-15, 32-38
 Bond energies, **2**, 49-109; **4**, 29-30, 45, 58
 Bond stability, fluorocarbon-metal complexes, **1**, 153-154

Bonding

carboranes, **3**, 307-308
 cyclic conjugated ligands, **5**, 94-100
 cyclobutadiene complexes, **4**, 101-102
 cyclooctatetraene complexes, **4**, 375-376
 diene complexes, **5**, 100-105
 metal carbonyls, **2**, 176-177; **3**, 185
 organolithium compounds, **3**, 371-380
 pseudohalides, **5**, 181-193
 valence tautomerism, **4**, 357-360, 378-379
 Boracyclanes, **2**, 258-286, 310
 Boranes, **3**, 283, 305-386
 Boron
 heterocycles, **2**, 257-322
 organic derivatives, **4**, 309-324
 Butadiene complexes, **1**, 2-5, 15, 29; **3**, 92, 103

C

Carbonylation of organic substrates, **2**, 3-9; **5**, 230-231
 Carbonylmetal anions, **1**, 178-184; **2**, 157-250
 Carboranes, **3**, 315-354
 Catenation in Group IV compounds, **1**, 50, 90-91; **4**, 1-84
 Chromium carbonyl derivatives, **2**, 182-202; **3**, 196-213
 Cobalt carbonyl derivatives, **2**, 235-249; **3**, 237-243; **4**, 243-266
 π -Complexes
 infrared spectra, **1**, 257-307
 NMR data, **3**, 47-156
 Conjugate addition of Grignard reagents to aromatic systems **1**, 221-237
 Cyanates, organometallic, **5**, 208-210
 Cyanides, organometallic, **5**, 201-207
 Cyclic boron compounds, **2**, 257-322
 Cyclic hydrocarbon complexes, **1**, 239-311; **3**, 47-156; **4**, 353-384
 Cyclic silicon compounds, **1**, 90-137

Cyclobutadiene, **4**, 96-99
 complexes, **4**, 95-141
 π -Cyclobutenyl complexes, **4**, 107-108
Cycloheptadiene complexes, **3**, 99; **4**,
 364-365
 π -Cycloheptadienyl complexes, **4**, 364-365
Cycloheptatriene complexes, **3**, 99; **4**,
 355-363
Cycloheptene complexes, **4**, 365-366
 π -Cycloheptenyl complexes, **4**, 365
Cyclohexadiene complexes, **3**, 97-98
 π -Cyclohexadienyl complexes, **3**, 129-132,
 149
Cyclooctadiene complexes, **2**, 38-39; **4**,
 369-375
Cyclooctatetraene complexes, **1**, 5-31,
 306-307; **2**, 40-41; **3**, 99-100, 161; **4**,
 375-380
Cyclooctatriene complexes, **3**, 100, 156; **4**,
 381-383
Cyclooctene complexes, **4**, 383-384
Cyclopentadienones, **2**, **4**; **5**, 101-104
Cyclopentadiene complexes, **1**, 23-25, 31-
 33, 36; **3**, 94-96
 π -Cyclopentadienyl complexes, **1**, 256-291;
 2, 366-404; **3**, 114-127, 212-213; **5**,
 94-98
Cyclopropane complexes, **3**, 26; **5**, 112-114
Cyclopropenyl complexes, **2**, 355
Cyclosilanes, **1**, 93-136; **4**, 7-11, 31-35

D

Decaborane (14), **3**, 302-305
Diarsine complexes, **3**, 195, 204-211, 230-
 231; **4**, 187-189
Diboranes, **3**, 265-290
Diene-metal complexes, **1**, 1-43; **3**, 105
Dinegative ions from aromatic hydro-
 carbons, **2**, 118-119, 132-152
Diolefin complexes, **3**, 54-63
Dipyridyl complexes, **3**, 200-213
Disilanes, **1**, 106-110, 129-134
Duroquinone complexes, **2**, 18-24; **5**, 124

E

Effective atomic number, **1**, 177; **2**, 169-170;
 3, 182

Electron diffraction
 organoarsenic compounds, **4**, 210-212
 organosilicon compounds, **5**, 39, 192
Electron spin resonance (ESR)
 aromatic hydrocarbon anions, **2**, 145-151
 organoarsenic compounds, **4**, 223
Electronic structures of alkali-metal-aro-
 matic hydrocarbon adducts, **2**, 115-152
Ethyl compounds, **3**, 16-21
Ethylene, complexes, **2**, 329; **3**, 48-49
 oxidation to acetaldehyde, **5**, 321-352
Exchange reactions
 diboranes, **3**, 266-267, 274
 metal carbonyls, **3**, 192-193
 organolithium compounds, **3**, 381-383
 studies by NMR, **3**, 156-159

F

Ferrocene, **1**, 266-267; **5**, 94
Ferrocenes, substituted, **2**, 369-379; **3**, 114,
 127-129, 135-149; **4**, 33, 220
Fluorocarbon-transition metal complexes,
 1, 143-220; **3**, 26-31, 43-46; **5**, 125-
 128, *see also* Pentafluorophenyl-metal
 compounds, Perfluoroalkyl complexes,
 Perfluorovinyl complexes
Fulminates, organometallic, **5**, 218
Fulvene complexes, **1**, 36-37

G

Germanium
 catenated derivatives, **4**, 38-47
 nitrogen compounds, **3**, 398-412
 sulfur derivatives, **5**, 52-92
Grignard reagent, **1**, 152, 228-237; **3**, 518;
 4, 280-285
Group IV
 catenation, **1**, 90-91; **4**, 1-84
 nitrogen compounds, **3**, 397-443
 sulfur compounds, **5**, 1-92

H

Heats of formation of organometallic com-
 pounds, **2**, 71-95
Heterocyclic compounds
 arsenic, **4**, 151-197
 boron, **2**, 257-321

Heterocyclic compounds—*cont.*

- metallo-rings, **5**, 122-124
- sulfur, **5**, 4-7, 26-37
- Hydride complexes, **3**, 195-196, 211, 236-246
- Hydroboration, **2**, 275-280; **3**, 270, 276-278
- Hydroformylation, **4**, 255
- Hydrogen, migration in diene complexes, **1**, 14-15, 21, 42
- Hydrostannation, **1**, 56, 63-65, 67

I

Infrared spectra

- π -complexes, **1**, 239-316
- cyclobutadiene complexes, **4**, 118
- diboranes, **3**, 289
- diene-iron tricarbonyls, **1**, 10-11, 30
- Group IV compounds, **4**, 24-26, 44, 58, 71; **5**, 41
- metal carbonyls, **3**, 187-190
- organoarsenic compounds, **4**, 220-222
- organolithium compounds, **3**, 374-375
- organotin compounds, **5**, 145-158
- pseudohalogen compounds, **5**, 178-179
- Insertion reactions, **4**, 258-265; **5**, 225-319
- Iridium carbonyl derivatives, **3**, 244-247
- Iron carbonyl
 - alkyne complexes, **1**, 37-43
 - anions, **1**, 37-38; **2**, 218-233
 - diene complexes, **1**, 1-37
 - phosphine derivatives, **3**, 224-226, 232-235
- Isocyanates, isocyanides, isoselenocyanates, and isothiocyanyates, organometallic, **5**, 182-219

L

- Lead compounds, **3**, 440-443; **4**, 63-77; **5**, 57-80
- Lewis acid complexes, **5**, 196
- Lewis base complexes, **3**, 181-252; **5**, 197
- Ligand displacement, **1**, 3-4, 24-29; **4**, 246-253
- Ligand exchange, **2**, 10-12; **4**, 108-111
- Lithium, organo derivatives, **3**, 365-393; **4**, 269-280

M

- Manganese carbonyl derivatives, **2**, 202-218; **3**, 213-223
- Mercury, organo derivatives, **4**, 289-309
- Metal-carbon bond strength, **2**, 49-110
- Metal carbonyl anions, **2**, 157-250
- Metal carbonyls
 - bond energies, **2**, 109-110
 - fluorocarbon derivatives, **1**, 180-184; **5**, 125-128
 - hydrides, **1**, 181
 - Lewis base complexes, **3**, 181-252
 - structures, **5**, 128
- Metallo-ring systems, **5**, 120-124
- Metal-metal bonds, **3**, 183-184, 251-252; **5**, 15-16
- Microwave spectra, **4**, 210-211; **5**, 40, 191
- Molecular orbital theory
 - π -allyl complexes, **2**, 333-335
 - hydrocarbon anions, **2**, 132-135
- Molybdenum carbonyl derivatives, **2**, 182-202; **3**, 196-213
- Mössbauer spectra, **1**, 6, 7

N

- Neocarborane, **3**, 335-336, 353
- Nickel carbonyl derivatives, **2**, 3-30, 249-250; **3**, 247-250
- Niobium carbonyls, **2**, 182
- Nitrogen compounds of Group IV, **3**, 397-443
- Nitrosyl complexes, **3**, 215-216, 229-230, 240-241
- Nuclear magnetic resonance (NMR)
 - allyl complexes, **3**, 71-91
 - arene complexes, **3**, 150-154
 - boranes, **3**, 289-290, 297-303
 - π -complexes, **3**, 47-156
 - σ -complexes, **3**, 4-47
 - cyclobutadiene complexes, **4**, 118
 - ferrocenes, **3**, 127-129, 135-149
 - fluorocarbon derivatives, **1**, 206-212; **3**, 26-31, 35, 43-47
 - Group IV compounds, **4**, 28-29, 44-45, 88; **5**, 41-42
 - organoarsenic compounds, **4**, 222-223
 - organolithium compounds, **3**, 381-383

O

- Olefin oxidation with palladium(II) catalysts, **5**, 321-352
 π -Olefin complexes, **3**, 47-156
Organoarsenic compounds, **4**, 145-229
Organoboranes, **2**, 106-107, 258-261
Organoboron compounds, **4**, 309-324
Organogermanium compounds
 catenation, **4**, 38-47
 nitrogen derivatives, **3**, 398-412
Organolead compounds, **3**, 440-443; **4**, 63-77
Organolithium compounds, **3**, 365-393; **4**, 269-280
Organomagnesium compounds, **4**, 280-289
Organomercury compounds, **4**, 289-309
Organometallic pseudohalides, **5**, 169-224
Organometallic reaction mechanisms, **4**, 268-340
Organonitrogen compounds, Group IV, **3**, 397-443
Organosilicon compounds, **2**, 106-107; **4**, 2-38, 324-339; **5**, 1-92
Organosilyllithium compounds, **1**, 98, 129-130
Organostannoxanes, **5**, 159-165
Organosulfur compounds, Group IV, **5**, 1-92
Organotellurium compounds, Group IV, **5**, 81-83
Organothallium compounds, **3**, 158-159
Organotin compounds, **3**, 413-439; **4**, 47-63, 324-339; **5**, 137-167
Organotin hydrides, **1**, 47-85
Osmium carbonyl derivatives, **3**, 236-237

P

- Palladium carbonyl complexes, **3**, 250-251
Palladium chloride, oxidation of ethylene, **5**, 321-352
Pentaboranes, **3**, 297-302
Pentafluorophenyl-metal compounds, **1**, 145-195; **3**, 43
Perfluoroalkyl complexes, **1**, 145-216; **2**, 250; **3**, 26-35
Perfluorovinyl complexes, **1**, 148-173, 211-214; **3**, 43-45

- Perphenylated cyclosilanes, **1**, 94-102, 117-132
Phosphine complexes, **3**, 195-196, 201-251, 281-283, 331-332
Polygermanes, **4**, 38-47
Polyplumbanes, **4**, 65-77
Polysilanes, **1**, 93-105, 117-136; **4**, 3-38
Polystannanes, **1**, 50; **4**, 48-63
Platinum complexes, **3**, 26, 48, 251; **5**, 113
Pseudohalides, organometallic, **5**, 169-224

R

- Radical anions, **2**, 117-152
Raman spectra, **1**, 251-254; **4**, 24, 44, 58, 71, 220
Reaction mechanisms, organometallic, **4**, 268-340
 carbon monoxide exchange, **3**, 192-193
 organoboron compounds, **4**, 309-324
 organocobalt carbonyls, **3**, 242
 organolithium compounds, **3**, 387-393; **4**, 269-280
 organomagnesium compounds, **4**, 280-289
 organomercury compounds, **4**, 289-309
 organosilicon compounds, **4**, 324-329
 organotin compounds, **1**, 63-84; **4**, 324-329
 substitution in metal carbonyls, **3**, 196, 207-208, 219-220
Rhenium carbonyl derivatives, **2**, 202-218; **3**, 223-224
Rhodium carbonyl derivatives, **2**, 234; **3**, 243-244
Ruthenium carbonyl derivatives, **2**, 218; **3**, 235-236

S

- Silicon, organo derivatives, **4**, 2-38; **5**, 1-92
Silyl derivatives, **1**, 102-117
Spectroscopy, *see* Electron spin resonance, Infrared, Mössbauer, Nuclear magnetic resonance, Raman, and Ultraviolet spectra
Sulfur-containing complexes, **3**, 206-244
Structures of organometallic complexes, **5**, 93-135

T

- Tantalum carbonyls, **2**, 182
Technetium derivatives, **2**, 202-206
Tetraboranes, **3**, 294-297
Tin, organo compounds, **1**, 47-85; **3**, 413-439; **4**, 47-63, 324-339; **5**, 54-81
Transition metal complexes
 π -complexes, **1**, 239-316; **3**, 47-156
 σ -complexes, **3**, 4-47
 cyclobutadiene, **4**, 95-141
 cyclopentadiene, **2**, 366-404
 7-membered carbocyclic hydrocarbons, **4**, 354-368
 8-membered carbocyclic hydrocarbons, **4**, 369-384
Transmetallation, **1**, 148-149
Trimethyltin derivatives, **5**, 146-148, 151-156
Tropone complexes, **1**, 42-43; **4**, 363

- Tropylium cation, **1**, 302-303
 complexes, **4**, 354-363
Tungsten carbonyl derivatives, **2**, 182-190;
 3, 196-213

U

- Ultraviolet spectra
 arsines, **4**, 225-227
 cyclobutadiene complexes, **4**, 118
 Group IV compounds, **4**, 26-28, 44, 71
 pseudohalides, **5**, 180-181

V

- Valence tautomerism, **3**, 159-161; **4**, 357-360, 378-379
Vanadium carbonyl derivatives, **2**, 178-181;
 3, 195-196
Vibrational spectra of π -complexes, **1**, 239-316